

Gerardine G. Botte and Madhivanan Muthuvel

Introduction

Energy consumption in the world has increased significantly over the past 20 years. In 2008, worldwide energy consumption was reported as 142,270 TWh [1], in contrast to 54,282 TWh in 1973; [2] this represents an increase of 262%. The surge in demand could be attributed to the growth of population and industrialization over the years. In 2009, energy consumption was reported as 140,700 TWh, a slight decrease (1.1%) when compared to 2008 due to the world financial crisis [1], while in 2010 there was a rise in the consumption to 149,469 TWh, due to the recovery of the economy at that time [3]. Conversely, the total supply of energy in the world had caught up with the consumption as shown in Table 38.1 [2, 4]. Approximately 10–14% of the total energy supply in the world is delivered as electric energy. In addition, the amount of power supplied by renewables had increased over the years, from 37 TWh in 1973 to 612 TWh in 2008 (as shown in Table 38.1), which represents a growth of 94%. However, the total amount of energy available from renewables based on current technology could reach up to 834,280 TWh (distributed as: 53.2% solar, 20.0% wind, 16.7% geothermal, 8.4% biomass, and 1.7% hydropower); [5] that is, 5.7 times the world energy supply in 2008. Nevertheless, renewable sources of energy such as solar and wind are intermittent and only abundant in certain regions, which causes a limitation on the use and distribution of such sources of energy. An undersized world energy surplus (based on a total energy balance including supply, consumption, and losses) is usually reported annually; a comprehensive analysis is presented in the literature [2].

Given the increase in energy consumption as the world's population grows, the scarcity of traditional energy supplies (i.e., petroleum, oil, and gas), and the environmental impact caused by conventional power generation systems, it has become imperative to utilize unconventional energy sources and renewables, and to redesign traditional processes to make them more energy efficient. Within this context, energy storage and conversion play a significant role. Energy storage refers to devices, or physical media, that collect different types of energy to be used at a later time. Perhaps the use of devices to accumulate energy is the most popular way, as it brings to mind the term "batteries," which has become extremely important with the spiraling growth of modern electronic applications. Indeed, batteries are a way to store energy. Batteries are unique devices, as the energy that is stored is chemical, but delivered as electrical. That is, batteries play a dual role: they store chemical energy, which is then delivered or converted directly into electrical energy when needed (we will return to this definition later). The definition of energy storage also includes physical media, which can be easily related to fuels (e.g., gasoline, diesel, hydrogen). Fuels are ways to store chemical energy that needs to be conventionally converted into electrical energy quite differently than the way batteries do it. Traditional power generation involves heat engines (e.g., turbines). In this process, a fuel is combusted to release thermal energy, the thermal energy is then transformed into kinetic energy through a rotor (i.e., using a turbine), and finally the kinetic energy is transformed into electrical energy by an electrical generator. The efficiency of the conventional process to convert chemical energy into electrical energy is limited by the Carnot cycle and is much lower than the efficiency of batteries.

There are different ways to store energy: chemical, biological, electrochemical, electrical, mechanical, thermal, and fuel conversion storage [6]. This chapter focuses on electrochemical energy storage and conversion. Traditionally, batteries, flow batteries, and fuel cells are considered as electrochemical energy storage devices. However, the

G.G. Botte (✉) • M. Muthuvel
Department of Chemical and Biomolecular Engineering,
Center for Electrochemical Engineering Research, Ohio University,
Athens, OH, USA
e-mail: botte@ohio.edu

authors believe that with the growth of renewable energy and intermittent energy sources, the concept of electrochemical energy storage can be extended to the electrochemical synthesis and production of fuels, chemicals, petrochemicals, etc. The vision of the approach is shown in Fig. 38.1 [7]. For example, the inspiration for the hydrogen economy is to use hydrogen as an energy carrier. The intention is to produce hydrogen through water electrolysis (electrochemical synthesis of hydrogen from water) by using electricity (electrical power) from intermittent (i.e., not available all the time) renewable power generation devices, such as solar panels

Table 38.1 Energy and power supply in the world

Year	Energy (TWh)	Power (TWh)	Fraction of energy supplied as power (%)	Power from renewables ^a (TWh)	Fraction of power from renewables (%)
1973	71,117	6,116	9	37	0.6
1990	102,569	11,821	12	277	2.3
2000	117,687	15,395	13	303	2.0
2001	118,147	15,502	13	301	1.9
2002	120,451	16,104	13	340	2.1
2003	124,675	16,688	13	361	2.2
2004	129,568	17,476	13	404	2.3
2005	133,602	18,258	14	450	2.5
2006	136,893	18,971	14	481	2.5
2007	139,390	19,804	14	561	2.8
2008	143,851	20,181	14	612	3.0

Sources

For 1973: IEA [2]

For 1990–2008: Energimyndigheten [4]

^aIncludes geothermal, solar, wind, combustible renewables and waste, and heat

and wind turbines. This way, hydrogen could be used to produce electricity when the intermittent source of electricity is not available, and to distribute the energy to remote sites. Conversely, the intention is to produce electricity by using hydrogen as the fuel in devices called fuel cells (we will return to this definition later). With this in mind, the vision of Fig. 38.1 is broader than the concept of the hydrogen economy. The final goal is to use intermittent and renewable sources of electricity (which represents 5.7 times the supply of energy in the world) to transform different feedstock into fuels, chemicals, petrochemicals, etc. That is, intermittent energy sources are used to store energy as products, commodities, or fuels via electrochemical synthesis.

In this chapter, the authors outline the basic concepts and theories associated with electrochemical energy storage, describe applications and devices used for electrochemical energy storage, summarize different industrial electrochemical processes, and introduce novel electrochemical processes for the synthesis of fuels as depicted in Fig. 38.1.

Basic Concepts

There are some important terminologies and fundamental theories associated with electrochemistry and electrochemical engineering. Electrochemical engineering is the branch of engineering dealing with the technological application of electrochemical phenomena. Electrochemical engineering evolved from industrial electrochemistry, which was defined in the early years as [8, 9] “the application of electric current

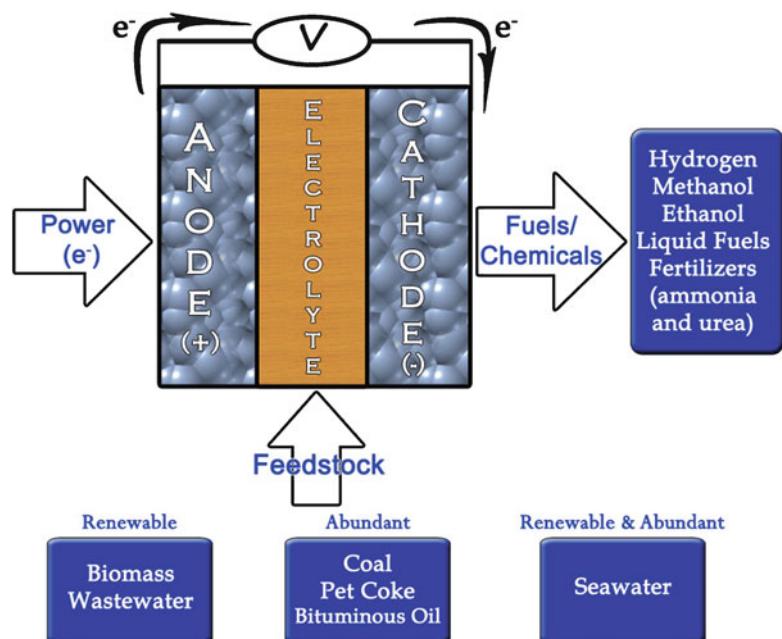


Fig. 38.1 Electrochemical synthesis of fuels, chemicals, and petrochemicals from different feedstocks [7]. Within the vision electrical power could be supplied from different sources, however, the concept creates the ideal platform to use renewable electrical energy from solar panels and wind turbines

to the chemical and metallurgical arts.” In this section, terminologies that are pertinent to the electrochemical energy storage devices are described.

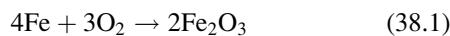
The basis for a traditional electrochemical energy storage system (batteries, fuel cells, and flow batteries) and the extended electrochemical energy storage concept presented in Fig. 38.1, known as electrosynthesis, is the electrochemical cell. An electrochemical cell consists of a case, an anode, a cathode, an electrolyte, and current collectors (as shown in Fig. 38.1). Electrochemical cells allow the direct conversion of chemical energy into electrical energy (galvanic cells or spontaneous cells) or vice versa, the direct conversion of electrical energy into chemical energy (electrolytic or electrolysis cells). Traditional electrochemical energy storage devices, such as batteries, flow batteries, and fuel cells, are considered galvanic cells. The approach depicted in Fig. 38.1, electrosynthesis reactor, is defined as an electrolytic or electrolysis cell. Electrochemical cells can be electrically connected in series, in parallel, or other configurations according to the needs of particular processes or applications.

The basis for the direct conversion of chemical to electrical energy, or vice versa, is the electrochemical reaction. An electrochemical reaction is a heterogeneous chemical process involving the transfer of electrons to or from an electrode (generally a metal, carbon, or electrically conducting material). It is important to mention that electrochemical reactions take place only on the electrode surface; this distinguishes an electrochemical system from a traditional chemical reactor.

Within this context, other important definitions are presented in subsequent sections. Additional definitions, thermodynamics, transport mechanisms, and electrokinetic models can be found elsewhere [10–13].

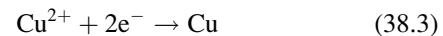
Oxidation

The removal of electrons from an element or ion, even if the element is part of a compound, during a chemical reaction is known as an oxidation reaction. Corrosion of an iron sheet, also known as rusting, is an electrochemical process. The rusting of an iron sheet is a good example of an oxidation reaction, where the elemental iron is oxidized to ferric oxide (Fe_2O_3) by oxygen present in the electrolyte (38.1). The oxidation reaction for iron is shown in (38.2) where the elemental iron losses three electrons to form ferric (Fe^{3+}) ion. The rusting of iron will be accelerated in an acid electrolyte.



Reduction

The reduction process is also related to transfer of electrons, where electrons are added to either the element or ion during the chemical reaction. For example, electroplating of copper metal on any electrically conducting surface is possible by the reduction of cupric (Cu^{2+}) ions found in the plating solution to elemental copper, by accepting two electrons provided by applied current supplied through the electrodes.



Anode

There are two established configurations for the electrochemical cells or systems: three-electrode and two-electrode systems. Generally, the two-electrode configuration is used in the commercial electrochemical devices, as shown in Fig. 38.1. In this two-electrode configuration, the electrochemical system consists of an anode, a cathode, and an electrolyte. The anode is the electrode where the oxidation reactions take place and it is connected to the positive terminal of the power supply unit. In order for the electrochemical oxidation reaction to take place on the anode, the anode has to be an electrically conducting material. Anode materials can be either insoluble or soluble substances depending on the electrochemical system. In the electroplating of precious metals, such as platinum, the anode material is made of platinum which is insoluble in the plating solution. On the other hand, for nickel electroplating, nickel sheet is used as the anode, which dissolves into the plating solution as nickel ions. The nickel ions eventually reduce as metallic nickel on the cathode electrode.

Cathode

On the other hand, the reduction reactions, such as (38.3), will take place at an electrode known as the cathode. The cathode electrode is connected to the negative terminal of the power supply unit. Similar to the anode material, the cathode material should also be electrically conducting so that the electrochemical reaction (reduction reaction) can take place. Generally, insoluble materials have been used as the cathode for the electrochemical systems. In the case of chrome plating on steel materials, the steel is the cathode electrode during the electroplating process.

The three-electrode system contains a working electrode, a counter electrode, and a reference electrode (will be discussed later). Either the working or the counter electrode could act as a cathode or an anode. The term working electrode is used to define the electrode that will be exposed

Table 38.2 Examples of different electrolytes used in electrochemical energy storage technologies and electrosynthesis

Electrolyte system	Supporting salt	Solvent	Conductivity (mS/cm)	Applications and details
1 M LiPF ₆ in EC/DMC (50:50 wt. %)	LiPF ₆	Organic solvents—EC and DMC	10.7 (at 25°C) [15]	Lithium ion batteries. No water should be present in the system. Nonaqueous electrolyte
H ₂ SO ₄ (30 wt. %)	H ₂ SO ₄	Water	730 [14]	Lead acid batteries and electroplating (low concentrations of H ₂ SO ₄). Aqueous electrolyte
0.1 M KOH	KOH	Water	21.3 (at 25°C) [19]	Electrolytic systems and electrodeposition. Aqueous electrolyte
KOH (29.4 wt. %)	KOH	Water	540 [14]	Alkaline battery. Aqueous electrolyte
EC/PC/LiClO ₄ /PAN (38/33/8/21) (mol%) Solid polymer electrolyte	LiClO ₄	EC, PC	1.7 (at 20°C) [16]	Lithium polymer battery. This is a solid polymer electrolyte
PC/LiClO ₄ /2p-MC-DBS/PEGPM (81.0/7.5/0.9/10.6) (wt. %)	LiClO ₄	PC	4.6 (at 25°C) [16]	Lithium battery. Gel electrolyte in polymer matrix
Na ₃ AlF ₆ /AlF ₃ /CaF ₂ /Al ₂ O ₃ (81/11/5/3) (wt. %)	Al ₂ O ₃	Cryolite (Na ₃ AlF ₆)	2,130 (at 950°C) [17]	Aluminum electrolysis. Molten electrolyte
(Y ₂ O ₃) _{0.08} (ZrO ₂) _{0.92} Yttria-stabilized zirconia (YSZ)	Y ₂ O ₃	ZrO ₂	30 (at 800°C) [18]	Solid oxide fuel cells. This is a solid electrolyte, where yttria is doped in zirconia

EC ethylene carbonate; DMC dimethyl carbonate; PC propylene carbonate; PAN poly(acrylonitrile); 2p-MC-DBS 1,3:2,4-di(*p*-methoxycarbonylbenzylidene) sorbitol; PEGPM poly(ethylene oxide)—grafted poly(methacrylate)

a. Schmidt M, Heider U, Kuehner A, Oesten R, Jungnitz M, Ignat'ev N, Sartori P (2001) Lithium fluoroalkylphosphates: a new class of conducting salts for electrolytes for high energy lithium-ion batteries. *Journal of Power Sources* 97–8:557–560¹⁵

b. Dobos D, (1975) *Electrochemical Data*. Akademiai Kiado, Budapest¹⁴

c. Haynes WM, ed. (2011) *CRC Handbook of Chemistry and Physics*. 92nd Edition (Internet Version 2012). CRC Press/Taylor and Francis, Boca Raton, FL¹⁹

d. Gores HJ, Barthel JMG (1995) Nonaqueous electrolyte solutions: New materials for devices and processes based on recent applied research. *Pure and Applied Chemistry* 67:919–930¹⁶

e. Hives J, Thonstad J, Sterten A, Fellner P (1996) Electrical conductivity of molten cryolite-based mixtures obtained with a tube-type cell made of pyrolytic boron nitride. *Metallurgical and Materials Transactions B* 27:255–261¹⁷

f. Yamamoto O (2000) Solid oxide fuel cells: fundamental aspects and prospects. *Electrochimica Acta* 45:2423–2435¹⁸

to a detailed electrochemical analysis through the use of different polarization techniques [11]. The counter electrode is used to carry enough current that will not prevent or limit any of the processes taking place at the working electrode. The three-electrode cell configurations are typically used for detailed and fundamental understanding of electrochemical reactions [11]. However, they also find applications in sensors.

Electrolyte

In an electrochemical cell, the electrodes—anode and cathode—are immersed in a solution (liquid, gel, or solid); the solution is known as the electrolyte. The electrolyte provides the medium for the movement of the ions (mobility) between the anode and the cathode. The operation of an electrochemical cell functions as a closed electrical system. Externally, the current travels between the power supply unit and the electrodes through the electrically conducting wires (see Fig. 38.1). In the electrolyte (internally), the movement of ions between the anode and the cathode (current flows internally through the transport of the ions) will complete the electrical circuit for the electrochemical cell. That is the anode/electrolyte/cathode, and power supply complete the electric circuit.

The flow of the electrons through the external circuit is relatively fast due to the use of highly electrically conducting materials. The limitation in the flow of current in an electrochemical system is experienced usually through the internal media: anode/electrolyte/cathode due to the diffusion and migration of ions across the electrolyte. The electrolyte can be aqueous, nonaqueous, or molten salt solutions. The electrolyte can also be made of a solid mixture. A solution of sulfuric acid is one of the most commonly used aqueous electrolytes. A nonaqueous electrolyte is lithium perchlorate (LiClO₄) dissolved in propylene carbonate, which is used in the lithium batteries. For the production of metallic sodium, molten salt of sodium chloride is electrolyzed, where molten sodium chloride is the molten electrolyte. A good example for a solid electrolyte is yttria-stabilized zirconia (YSZ), which is a ceramic material used as solid oxide electrolyte in solid oxide fuel cells (SOFCs).

The electrochemical reactions taking place on the surface of the electrodes depend on the transport properties of the ions in the electrolyte medium. One of the important properties of the electrolyte is its ionic conductivity, which is affected by factors, such as temperature, supporting salt concentration, solvent, and pressure. Table 38.2 lists some of the different electrolytes used in the energy storage systems

Table 38.3 Classical separators, membranes, and diaphragms used in electrochemical energy storage technologies and electrosynthesis

Material	Type	Applications and details
Nafion (sulfonated tetrafluoroethylene-based fluoropolymer-copolymer)	Membrane	Chlor-alkali cell and proton exchange membrane fuel cell. Allows transport of cations, especially protons
Cellophane	Membrane	Nickel cadmium and silver oxide batteries. Provides gas barrier along with ion permeability
Polyethylene	Separator	Lead acid batteries. These separators with small pore size are used in heavy duty batteries and they provide longer life to the battery
Polypropylene	Separator	Lithium-based batteries. The separator is used in primary and secondary types of lithium batteries
Asbestos	Diaphragm	Chlor-alkali cell. This separator was used in the original design of chlor-alkali cell. The health problems associated with asbestos has restricted its application as separator
Teflon (polytetrafluoroethylene)	Diaphragm	Chlor-alkali cells and aqueous electrolysis. Chemically inert to acids, alkalis, and organic solvents

Sources: Linden [20]; Kuhn [83]

along with their conductivity. Usually aqueous electrolytes possess the highest ionic conductivity at room temperature. As shown in Table 38.2, the 30 wt. % sulfuric acid solution (aqueous electrolyte) used in the lead acid battery (LAB) has an ionic conductivity of 730 mS/cm [14]. The nonaqueous electrolyte used in commercial lithium ion (Li-ion) batteries consisting of 1 M LiPF₆ dissolved in the organic solvents of ethylene carbonate and dimethyl carbonate (50:50 wt. %) has an ionic conductivity of 10.7 mS/cm at 25°C [15]. Lithium batteries also use gel type electrolytes, such as PC/LiClO₄/2p-MC-DBS/PEGPM (81.0/7.5/0.9/10.6) (wt. %), where PC stands for propylene carbonate, 2p-MC-DBS means 1,3:2,4-di(*p*-methoxycarbonylbenzylidene) sorbitol, and PEGPM is poly(ethylene oxide) (PEO)—grafted poly(methacrylate). This gel electrolyte has an ionic conductivity of 4.6 mS/cm at 25°C [16]. The molten electrolyte used in the aluminum electrolysis process has alumina (Al₂O₃) mixed with CaF₂ and AlF₃ additives, which are dissolved in cryolite (Na₃AlF₆) solvent. The ionic conductivity for this molten electrolyte is 2,130 mS/cm at 950°C [17]. In SOFCs, zirconia (ZrO₂) doped with 8% of yttria (Y₂O₃), commonly known as yttria-stabilized zirconia, is used as the solid electrolyte. YSZ has an ionic conductivity of 30 mS/cm at 800°C [18]. The readers are requested to review the following literature for more details about transport processes in electrochemical systems and conductivity [10, 11].

Separator

In a divided electrochemical cell, an electrically insulated layer material is used to separate the electrode, electrolyte, and any products formed between the anode and the cathode side. This electrically insulated material is called the separator. The separators should be permeable to the ions present in the electrolyte to facilitate the completion of the electrical circuit. The different types of separators are membranes and

diaphragms. The membranes have a smaller pore size which will result in selective permeability of ions across the compartments. On the other hand, diaphragms are those separators that have larger pore size and permits transfer of many ions at higher flow rate across the compartment without leading to intermixing of electrolytes. In general, the distinction between membrane and diaphragm is blurred as some separators can be engineered to have different porosity and selectivity for permeation. A list of various commonly used separators (membranes and diaphragms) is listed in Table 38.3.

Reference Electrode

In a three-electrode cell system, a third electrode other than the anode and cathode, the reference electrode, is used. Reference electrodes are standard electrodes, which are chemically and mechanically robust, and their potential is expected to remain unchanged under most electrolytic conditions. In electrochemistry, one cannot measure the potential of an electrode, but the potential difference between two electrodes is measurable. If one of the two electrodes is a standard or reference electrode, then the potential of the other electrode can be determined in terms of the reference electrode. So, every time a potential value is assigned to an electrode, it is always expressed with respect to a reference electrode.

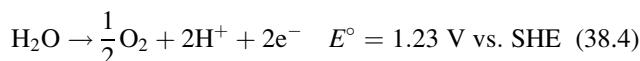
The standard hydrogen electrode (SHE) is the primary reference electrode and its potential is assigned a zero value (see section on “Standard Potential”). For example, consider an electrolytic system where deposition of copper is carried out using an electrolyte containing copper sulfate and sulfuric acid. At the anode, a water molecule is oxidized to oxygen and protons, whereas metallic copper is deposited at the cathode electrode. The following half cell reactions (anode and cathode reaction) with their standard reduction potential illustrate the electrolytic cell.

Table 38.4 Standard reduction potential for some electrochemical reactions

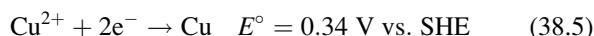
Reaction	E° (V)
$\text{Li}^+ + \text{e}^- \rightleftharpoons \text{Li}$	-3.0401
$\text{Na}^+ + \text{e}^- \rightleftharpoons \text{Na}$	-2.71
$\text{Al}(\text{OH})_3 + 3\text{e}^- \rightleftharpoons \text{Al} + 3\text{OH}^-$	-2.31
$\text{Te} + 2\text{e}^- \rightleftharpoons \text{Te}^{2-}$	-1.143
$\text{Ni}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ni}$	-0.257
$\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb}$	-0.1262
$\text{Fe}^{3+} + 3\text{e}^- \rightleftharpoons \text{Fe}$	-0.037
$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$	0.0000
$\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{NO}_2^- + 2\text{OH}^-$	0.01
$\text{Cu}^{2+} + \text{e}^- \rightleftharpoons \text{Cu}^+$	0.153
$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$	0.3419
$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$	0.7996
$\text{Pt}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pt}$	1.18
$\text{Au}^{3+} + 3\text{e}^- \rightleftharpoons \text{Au}$	1.498
$\text{F}_2 + 2\text{e}^- \rightleftharpoons 2\text{F}^-$	2.866

Source: Haynes [19]

Anode reaction:



Cathode reaction:



The secondary reference electrodes have been frequently used in the electrochemical systems because they are easier to construct and maintain than the SHE. One of the commonly used reference electrodes is the saturated calomel electrode (SCE), which has a potential of 0.242 V vs. SHE. Another reference electrode used in the acidic electrolytes has been the silver-silver chloride electrode and its potential is 0.197 V vs. SHE.

Standard Potential

The standard potential (E°) is related to an electrochemical reaction on the electrode surface at standard condition of 25°C and 1 atmospheric pressure. The standard potential for the reduction or oxidation reaction of the chemical substance present in the electrochemical system is valuable information principally to determine the possible reactions taking place in the system. In general, the standard potential is represented as the reduction potential for that reaction vs. the SHE. Table 38.4 contains the standard reduction potential of commonly used reactions.

The formation of hydrogen from protons is zero volts as the reaction is measured with respect to an SHE. The

standard reduction potential for lithium ion (Li^+) is -3.0401 V which is the least valued potential in Table 38.4. The most negative value of the standard reduction potential means that lithium (Li) is more likely to get oxidized into Li^+ ion. On the other hand, the reduction of the platinum ion (Pt^{2+}) to Pt (1.18 V) is more favorable than the Li^+ ion reduction.

Table 38.4 lists only a few reactions and its standard reduction potential, but a complete list for the standard reduction potential of various reactions can be found in the CRC Handbook for Chemistry and Physics [19]. The list of the standard reduction potential suggests thermodynamically which reaction would occur, or is feasible, in an electrochemical system. For example, a platinum electrode immersed in a solution containing 0.1 M Ni^{2+} in 1 M HCl will result in an open circuit potential greater than 0 V. Once the potential of the Pt electrode is shifted in the negative direction with respect to SHE, the reaction with most positive reduction potential will occur first. So, in this case the evolution of hydrogen (0 V vs. SHE) will occur even before the deposition of Ni on the Pt electrode (-0.257 V vs. SHE). On the other hand, by shifting the potential of the electrode in the positive direction, the reaction with least positive potential will occur first. If a gold electrode is immersed in a Cu^+ ion solution and the potential of the Au electrode was increased in the positive direction, then the oxidation of Cu^+ to Cu^{2+} (0.153 V vs. SHE) would take place before the gold electrode oxidizes (1.498 V vs. SHE). The table covering standard reduction potentials provides an opportunity to perform controlled and specific reactions on the electrode surface because each electrochemical reaction can be controlled by its potential.

Nernst Equation

The potential for an electrochemical reaction can be represented in terms of a thermodynamic quantity, the Gibbs free energy change. Equations (38.6) and (38.7) display the relationship between the Gibbs free energy change and the potential for the reaction at normal and standard conditions. Standard conditions are referred to temperature of 25°C and 1 atmospheric pressure with unit activity for the chemicals involved in the electrochemical reaction. The Gibbs free energy for the reaction taking place at conditions other than the standard condition is represented in (38.6).

$$\Delta G = -nFE \quad (38.6)$$

$$\Delta G^\circ = -nFE^\circ \quad (38.7)$$

where ΔG° and E° are the standard Gibbs free energy change and the standard reaction potential, respectively. On considering a simple electrochemical reaction at equilibrium as

given in (38.8), an oxidized species (O) takes up n electrons to form the reduced species (R).



From the basic thermodynamics, the Gibbs free energy for the above reaction can be written as

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_R}{a_O} \quad (38.9)$$

where R is the molar gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature (K), a_R and a_O are the activities for the reduced and oxidized species, respectively. On substituting the Gibbs free energy change from (38.6) and (38.7) to the (38.9), we obtain

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_R}{a_O} \quad (38.10)$$

The Nernst equation for an electrochemical reaction is represented by rearranging (38.10).

$$E = E^\circ + \frac{RT}{nF} \ln \frac{a_O}{a_R} \quad (38.11)$$

The potential of the reaction is dependent on the standard reduction potential (E°), and the activities of the oxidized and reduced species. The activity is a chemical thermodynamic term meaning effective concentration of the species in a mixture. The activity of the species is expressed as the product between the activity coefficient (γ) and the concentration of the species. Since, it is difficult to determine the activity of the species in an electrochemical reaction, the Nernst equation can be defined in terms of the species concentration (38.12).

$$E = E^\circ' + \frac{RT}{nF} \ln \frac{[O]}{[R]} \quad (38.12)$$

where the concentrations of oxidized and reduced species are $[O]$ and $[R]$, respectively, and E°' is the formal potential of the reaction. The formal potential is defined as the measured potential of the reaction when the ratio of the concentrations of oxidized and reduced species is unity. The following equation displays the relationship between the formal potential and the activity coefficient of the species.

$$E^\circ' = E^\circ + \frac{RT}{nF} \ln \frac{\gamma_O}{\gamma_R} \quad (38.13)$$

An electrode following the Nernst equation is referred to as the Nernstian system when the electrode potential changes because of the changes observed in the concentration of the species present in the electrochemical system.

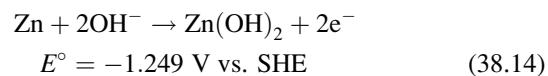
Alternatively, if the potential of an electrode does not follow the Nernst equation, then it is considered to be non-Nernstian system.

Cell Voltage

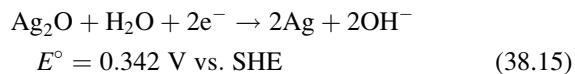
In a two electrode system, the potential difference between the anode and cathode electrodes is defined as the cell voltage. The term “potential,” which has been used extensively earlier, is only referred to as the potential difference observed between an electrode and a reference electrode. The cell voltage is denoted by V ; it also uses the same thermodynamic relation with the change in the Gibbs free energy as shown in (38.6). The units for cell voltage are volts (V), which is also the unit for the electrode potential.

As described earlier, there are two types of electrochemical cells, namely electrolytic and galvanic cells. In a galvanic cell, such as silver oxide-zinc battery, a primary battery system, the cell voltage can be determined using the anode and cathode electrode potentials. The anode, cathode, and the overall reactions for the silver oxide-zinc battery are given below [20].

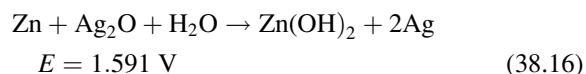
Anode reaction:



Cathode reaction:



Overall reaction:



At the anode electrode, the Zn is oxidized to zinc hydroxide in the presence of hydroxyl ions from the alkaline electrolyte and the silver oxide is reduced to silver at the cathode electrode. The overall reaction is the formation of zinc hydroxide and silver from zinc and silver oxide, which results in a generating cell voltage of 1.591 V. The voltage for the overall reaction was obtained by subtracting the standard potential of the anode reaction from the cathode reaction. This cell voltage is also known as the theoretical voltage for the battery [20]. The theoretical voltage of a battery represents the maximum cell voltage that can be attained by the battery. In practical applications, the theoretical voltage is very difficult to reach due to various factors, such as concentration, temperature, and transport of ions.

The influence of these factors leads to ohmic limitations, concentration limitations, surface limitations, and diffusion limitations during the operation of any galvanic system. For the silver oxide-zinc battery, even though it has the theoretical voltage of 1.591 V, the nominal voltage or voltage during practical application is only 1.5 V [20].

In the case of an electrolytic system, such as the electrolysis of water, the theoretical cell voltage required to split water into hydrogen and oxygen gases is 1.23 V. In the electrolytic system, the theoretical voltage is the minimum required voltage to initiate the electrochemical reaction and due to various factors the cell voltage has to be maintained more than the theoretical value in order to sustain the reaction. The key factors affecting the operation of electrolytic systems are the solution resistance, diffusion limitations faced by the ions at the electrode surface, occurrence of secondary or undesired reactions at the electrode surface, and even the resistance to the flow of electrons along the wire or electrical contact. Even though the theoretical voltage required for water electrolysis is 1.23 V, the commercial alkaline water electrolyzers operate between 1.7 and 1.9 V to compensate for the losses due to the above mentioned factors [21].

Faraday's Law

In an electrochemical reaction, electron transfer results in the formation of a new product or loss of a compound. The mass of the new product formed or the loss of the existing material is directly proportional to the number of electrons passed through the electrode. This is known as Faraday's law. The time rate of flow of electrons is known as current, and the number of electrons is referred to as charge (Q), and its units are coulombs (C).

$$m = \frac{Q \times M}{n \times F} \quad (38.17)$$

where m is the mass of the substance (g) formed or lost during the electrochemical reaction, M is the molar mass of the substance ($g/mole$), n is the number of electrons transferred per mole during the reaction, and F is the Faraday constant, which equals 96,485 C.

The mass of the material deposited or lost is directly related to the current passed through the electrochemical cell. If all the current supplied to the electrochemical cell is utilized for the expected reaction, then the Faraday efficiency is 100%. In most systems, however, part of the applied current results in undesired or secondary reactions and generates other products, which leads to lower than 100% in Faraday efficiency. The ratio of actual weight of the material formed to the theoretical weight based on that current is known as Faraday efficiency. In some places,

Faraday efficiency is also referred as Faradaic efficiency, coulombic efficiency, or current efficiency. Faraday's law is a valuable concept along with current efficiency to estimate the total current required for scaling up an electrochemical process, as it would lead to the calculation of the number of cells, electrodes, and energy consumption needed for the process.

The use of Faraday's law can be demonstrated with an electrolytic system, aluminum production. The production of aluminum is an energy consuming process and it is performed by electrolysis of molten salt of alumina (Al_2O_3). In the aluminum industry, the modern aluminum reduction cell system is supplied with a total current of 300 kA and a cell voltage of 4.2 V is maintained for every day operation [22]. The molar mass for aluminum (M) is 26.98 g/mol and the number of electrons (n) involved during the reduction reaction is 3. The total charge, the product of current and time, supplied for a day to the electrochemical cell for aluminum reduction is Q .

$$Q = \text{current} \times \text{time} = 300 \text{ kA} \times 24 \text{ h} \times 60 \text{ min} \times 60 \text{ s} \\ = 25,920 \times 10^6 \text{ coulombs}$$

Substituting the values for charge (Q), molar mass (M), number of electrons (n), and Faraday's constant in (38.17), we obtain the theoretical amount of aluminum produced per day using 300 kA of current. The theoretical aluminum calculated was 2,416 kg/day. According to the aluminum industry literature, the industry produces 2,308 kg of aluminum per day using a current supply of 300 kA [22].

The Faraday efficiency for the production of aluminum using the electrolysis process can be calculated using the above values. The current or Faraday efficiency for the aluminum reduction process was 95.5%. Energy consumption for the electrolysis process is defined as the product of the total charge supplied and the voltage maintained in the cell. For the production of aluminum, the energy consumption was calculated to be 13.1 kWh for every gram of aluminum produced.

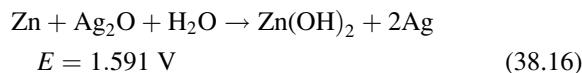
Battery Capacity

For battery systems, the total current which can be obtained from an electrochemical system in 1 h is termed as capacity. The units for capacity are ampere-hour (Ah). The theoretical capacity of a battery is dependent on the active material available as electrode with the internal resistance of the electrolyte not being taken into consideration. Using Faraday's law, the theoretical capacity for the electrode material is given as

$$C_e = 26.8 \frac{A - h}{eq - g} \frac{1}{M_e} \quad (38.18)$$

where the electrode material capacity is C_e (ampere-hour per gram) and M_e is the equivalent weight of the electrode material (grams per equivalent gram). The equivalent weight is represented by the molecular weight of the electrode material divided by the number of electrons transferred during the reaction [13].

For example, the silver oxide-zinc battery is composed of zinc as active material in the anode electrode and silver oxide is the active material in the cathode. The overall reaction for the battery is given in (38.16).



The equivalent weight for Zn (M_{Zn}) is 32.68 g/eq–g and the cathode active material, silver oxide, has an equivalent weight ($M_{\text{Ag}_2\text{O}}$) of 116 g/eq–g. Using (38.18), the theoretical capacity for anode electrode of the silver oxide-zinc battery can be calculated as $C_{\text{Zn}} = 820 \text{ mAh/g}$ and the cathode material has the theoretical capacity of $C_{\text{Ag}_2\text{O}} = 231 \text{ mAh/g}$.

Once the theoretical capacity of the electrode material is calculated, then the total capacity of the electrode can be obtained from (38.19).

$$C_T = C_e W_e \quad (38.19)$$

where C_T is the total capacity for the electrode (ampere-hour) and W_e is the weight of the electrode material (grams). The total capacity of both the electrodes will be calculated using the above equations; the lowest capacity is taken as the theoretical capacity of the battery system. If the weight of active material for the silver oxide-zinc battery is assumed to be 5 g, then the total capacity for Zn is $C_T = 4,100 \text{ mAh}$ and for Ag_2O is $C_T = 1,155 \text{ mAh}$. Since the theoretical capacity of the cathode material, silver oxide, is the limiting value, then the theoretical capacity for the silver oxide-zinc battery will be 231 mAh/g.

There is another equation used to determine the theoretical capacity of the battery system, which is based on the total quantity of electricity used in both the anode and cathode electrode [20].

$$C_T = \frac{1}{1/C_{e,\text{negative}} + 1/C_{e,\text{positive}}} \quad (38.20)$$

On using the equation for the silver oxide-zinc battery system, the theoretical capacity of this battery was found to be 180 mAh/g.

Energy Density

Energy density of a battery is determined by taking the product of the cell voltage and capacity of the battery. The

unit for the energy density is represented by watt-hour per gram (Wh/g). Energy density is also an important property as the capacity for the battery. The theoretical energy density for a battery system is represented as: [20]

$$\begin{aligned} \text{Theoretical energy density(Wh/g)} &= \text{Theoretical voltage(V)} \\ &\times \text{Theoretical capacity(Ah/g)} \end{aligned} \quad (38.21)$$

In the case of the silver oxide-zinc battery, the theoretical voltage is 1.591 V and the theoretical capacity determined in the previous subsection was 180 mAh/g. Using these values in the above equation, we obtain the theoretical energy density for the silver oxide-zinc battery as 0.286 Wh/g or 286 Wh/kg.

Electrokinetics

In the electrochemical systems, the rate at which reactions take place on the electrode surface depends on different properties such as electrode material, concentration of ions present in the electrolyte, mobility of the ions, and the concentration of ions at the electrode surface. At equilibrium, the ions in the electrolyte will cover the electrode surface based on their charge and form a layer known as double layer. The double layer is described as the combination of adsorbed ionic species and the layer of solvated ions over the surface of metal. Figure 38.2 shows the illustration of the metal/solution interface based on the geometric model. There are three established models, namely Helmholtz theory, Gouy-Chapman theory, and Stern theory, to elucidate the formation of the double layer over the metal surface.

The metal electrode immersed in an electrolyte is covered by adsorbed ions due to the excess charge on the metal surface. An imaginary line running through the centers of the adsorbed ions form the inner Helmholtz layer or plane. The outer Helmholtz layer or plane is the locus of centers of the nearest solvated ions. Beyond the outer Helmholtz layer, there are nonspecifically adsorbed ions which form a diffuse layer. The double layer in the electrolyte solution is composed of the inner and outer Helmholtz layers, and the diffuse layer. The thickness and composition of double layer will determine the surface overpotential. For ionic concentrations more than 0.01 M, the double layer thickness is expected to be less than $\sim 100 \text{ \AA}$ [11]. Surface overpotential (η_s) is expressed as the potential of the working electrode with respect to the reference electrode, which is placed just outside of the double layer. The term overpotential is defined as the difference between the measured potential and the equilibrium potential for that reaction.

Electrochemical reaction rates are defined in terms of the current density of the reactions, the concentration of ions in

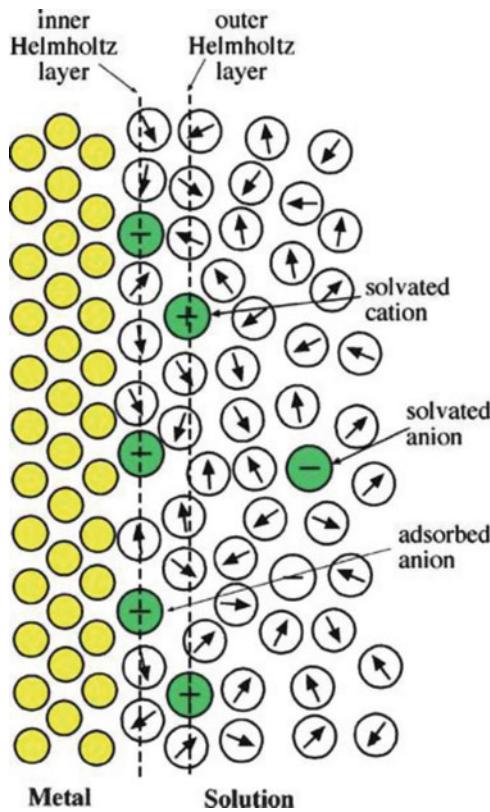


Fig. 38.2 Illustration of metal/solution interface to depict the presence of double layer [23]. The double layer is composed of adsorbed and solvated ions over the metal surface. The double layer has many layers; among those are the inner and outer Helmholtz layer

the electrolyte, and the overpotential. A classical way to relate these parameters is using the Butler-Volmer equation:

$$i = i_o \left[e^{((\alpha_a F/RT)\eta_s)} - e^{(-(\alpha_c F/RT)\eta_s)} \right] \quad (38.22)$$

where i_o is the exchange current (A), α_a and α_c are the transfer coefficients for the anodic and cathodic reactions, respectively, i is the current for the reaction (A), and η_s is the surface overpotential for the electrode.

For electrochemical reactions which are irreversible in nature, an approximation of the Butler-Volmer equation will lead to the Tafle equations (38.23) and (38.24). In the case where the anodic reactions are more applicable than cathodic reactions, then $a_a F \eta_s \gg RT$ and the Butler-Volmer equation is reduced to

$$i = i_o e^{((\alpha_a F/RT)\eta_s)} \quad (38.23)$$

Similarly, if the cathodic reactions are more applicable than the anodic reactions, then $a_c F \eta_s \gg RT$ and the Butler-Volmer equation is modified to

$$i = -i_o e^{(-(\alpha_c F/RT)\eta_s)} \quad (38.24)$$

Table 38.5 Various dielectric materials and their constants

Dielectric material	Dielectric constant (ϵ)
Air (dry, CO_2 free)	1.0005360
Aluminum oxide	9.34–11.54
Glass (Pyrex 7740)	5.0
Lead magnesium niobate	10,000
Lead titanate	~200
Mica (muscovite)	5.4
Polypropylene	2.3
Polystyrene	2.6
Potassium tantalate niobate (0°C)	34,000
Quartz (fused)	3.75
Tantalum pentoxide (α phase)	30–65
Teflon	2.1
Vacuum	1.000 (exact)
Water (liquid, 20°C)	80.1

Source: Haynes [19]

Capacitor

An electronic device, which is capable of storing electric charge, is defined as a capacitor. Capacitors can be used in place of batteries to store electrical energy and can also discharge the electrical energy during a relatively short duration. This device has two electrically conducting electrodes, which are separated by a nonconducting material. The nonconducting material is known as a dielectric, which is made of an insulator material.

The capacitor is classified as polarized and non-polarized based on the characteristic of the dielectric material. The non-polarized capacitors have ceramics and polymers as the dielectric materials, whereas oxides of aluminum and tantalum are used in the polarized capacitors. Polarized capacitors are generally referred to as electrolytic capacitors, which are electrochemical devices [23]. Each dielectric material has a characteristic value known as dielectric constant. Vacuum is dielectric and it has been used in the old-fashioned capacitors. The dielectric constant for vacuum is assigned a value of unity. Technically, the dielectric constant of a material is the ratio of the relative permittivity of the material to store the electrical energy, when voltage is applied, with respect to the storage capability under vacuum. Various dielectric materials and their constants are listed in Table 38.5.

Capacitance is the measure of the capacitor's ability to store the electrical energy for a certain potential difference across the electrodes. When a voltage is applied between the electrodes, the positive charges are collected in one electrode and the negative charges will be generated on the other electrode.

$$C = \frac{Q}{V} \quad (38.25)$$

Table 38.6 Comparison of the characteristics of few primary batteries

Characteristics	Zinc chloride (zinc-carbon)	Alkaline manganese dioxide	Zinc-air
Anode	Zn	Zn	Zn
Cathode	MnO ₂	MnO ₂	O ₂ (air)
Electrolyte	ZnCl ₂ (aqueous solution)	KOH (aqueous solution)	KOH (aqueous solution)
Open-circuit voltage (V)	1.6	1.5–1.6	1.45
Nominal voltage (V)	1.5	1.5	1.5
End voltage (V)	0.9	0.9	0.9
Operating temperature (°C)	–10 to 50	–20 to 55	0–50
Energy density at 20°C: button size (Wh/kg)	–	38	340
Energy density at 20°C: cylindrical size (Wh/kg)	85	125	–
Power density	Low to moderate	Moderate	Low
Self-discharge rate at 20°C (% loss per year)	7	4	3 (if sealed)

Source: Linden [20]

The ratio of electric charge divided by the potential difference is referred to as the capacitance of the capacitor. The units for the capacitance are Farads (F). Applying a potential difference of 1 V across the electrode plates when 1 coulomb of charge is stored on the electrodes is referred to a capacitance of 1 farad for that capacitor. Capacitors for typical industrial use are manufactured in the range of μF to mF.

Electrochemical Energy Storage Technologies

Classical electrochemical energy storage technologies include batteries, flow batteries, and fuel cells. This section provides an overview of the different technologies; additional literature is recommended [13, 20, 24–32]. In addition, this section also includes a synopsis of super capacitors or electrochemical double layer capacitors (EDLCs), which could be considered advanced electrochemical energy storage systems.

Batteries

The most commonly known electrochemical energy storage device is a battery, as it finds applications in all kinds of instruments, devices, and emergency equipment. A battery's principal use is to provide immediate power or energy on demand. A battery is an electrochemical device where energy from a chemical reaction of the reactants is directly converted into electrical energy. There are two types of batteries: primary and secondary. In primary batteries, the chemical compounds as reactants are consumed to form electrical energy and products, but the products cannot be transformed back into reactants with the use of external electric power. On the other hand, secondary batteries can be recharged by producing the reactants from the products with the help of external

electrical energy. Secondary batteries are also known as rechargeable batteries.

The batteries that come under the primary batteries are zinc chloride, alkaline (zinc-manganese dioxide), and zinc-air. Secondary batteries consist of LAB, nickel-cadmium (Ni-Cd), nickel metal hydride (Ni-MH), and lithium ion (Li-ion) battery. Other kinds of batteries, such as a flow battery, redox battery, and sodium nickel chloride battery, are the latest improvements in the area of batteries. In batteries, the convention is that the anode is considered to be the negative terminal and the cathode is considered to be the positive terminal. The electrochemical reactions of these batteries at both the positive and negative terminals, along with a brief description of their properties, are presented next.

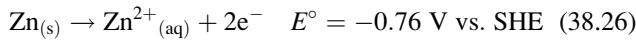
Primary Batteries

The characteristics of the few primary batteries that are discussed in this section are listed in Table 38.6. The table provides information on the electrodes, electrolyte, cell voltage, operating temperature, energy and power density, self-discharge rate, advantages, and limitations for each battery.

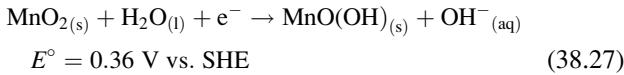
Zinc-Chloride

This battery is one of the first kinds to be commercially sold, and it is an improved version of the zinc-carbon battery. A can, or the container of the battery that is made of Zn, will act as the negative terminal (anode) of the battery. A carbon rod is the positive terminal (cathode), which is covered by a manganese dioxide paste. Next to the manganese dioxide paste is a layer of zinc chloride electrolyte, which is separated by a paper separator. There are two types of separators used in the Zn-chloride batteries, gelled paste and a special paper coated with gelled paste or cereal. The electrochemical reactions for zinc chloride battery are given below:

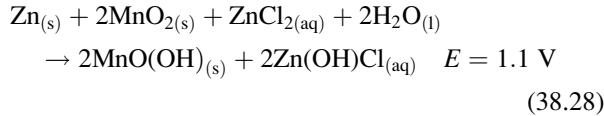
Anode reaction



Cathode reaction



Overall reaction



At the anode electrode, Zn is oxidized to Zn^{2+} ions and manganese dioxide is reduced to manganese oxyhydroxide (MnO(OH)) at the cathode electrode. The cell voltage for the overall reaction is 1.5 V.

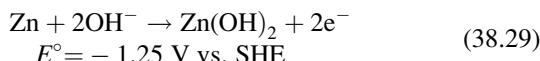
The zinc chloride batteries are used in flashlights, penlight, photoflash, smoke detectors, and electronic applications. Commercially, these batteries are manufactured in cylindrical form in different sizes, such as AA, C, D, and F. Household flashlights use sizes C and D Zn-chloride batteries, whereas size AA is normally reserved for penlight, photoflash, and electronic applications [20].

One of the limitations of the Zn-chloride batteries is its high self-discharge rate which means that the Zn-chloride battery will lose its capacity even if it were left idle. Additionally, these batteries are known to have high gassing rates; that is, the Zn-chloride batteries produce more gas from the secondary reactions due to the presence of contamination in the Zn anode [20]. In general, the Zn-chloride battery is not able to keep up with the growing electronic industry because the Zn-chloride battery has lower power density due to the small size and the lack of rechargeable capabilities.

Alkaline Batteries

The electrode material used for the alkaline battery is similar to the Zn-chloride battery with the exception of the potassium hydroxide (KOH) electrolyte. The anode electrode for the alkaline battery is zinc powder, which is mixed with KOH to form a gel. The cathode electrode is manganese dioxide. The following equations illustrates the electrochemical reactions taking place in an alkaline battery: [33]

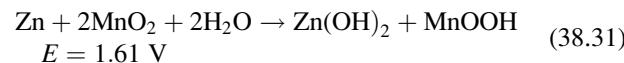
Anode reaction



Cathode reaction



Overall reaction



The theoretical cell voltage for an alkaline battery is 1.61 V, but the optimum voltage will be closer to the zinc-based primary batteries (1.5 V). The purity of the electrode material and its activity determines the initial open-circuit voltage of the alkaline battery. These aspects lead to the lowering of the optimum open-circuit voltage of the alkaline battery to 1.5 V from the theoretical cell voltage (1.61 V).

Alkaline batteries have higher energy density and longer operation time in comparison with the inexpensive zinc-carbon and zinc chloride batteries. These batteries are popular for usage in various applications because of their relatively low cost, higher energy and power density, and good portability for providing power to portable electronic devices. Alkaline batteries are manufactured in both cylindrical and miniature sizes.

The alkaline batteries experience similar kinds of limitations as those of zinc chloride batteries. The corrosion of the Zn anode material is also prevalent in the alkaline battery, which essentially lowers the battery capacity and eventually degrades the life of the battery. Zinc in the environment of an alkaline electrolyte is active and it can reduce water into hydrogen gas. The presence of hydrogen gas will increase the internal pressure of the battery, and can cause leakage of the electrolyte and even possible explosion of the battery [34]. In addition, these alkaline batteries are the primary batteries which cannot be recharged to extend their life. In recent years, various research activities have been focused to convert the alkaline battery into a rechargeable battery by the addition of different active materials to the alkaline manganese dioxide cathode [35–38].

Zinc-Air

Zinc-air batteries are well known as the batteries used in hearing aid devices. A cross-sectional view of a Zn-air battery is displayed in Fig. 38.3. The voltage for this battery is produced from the oxidation of zinc in air. As the oxygen from the air is the active material on the cathode side, the cathode can (Fig. 38.3) has holes for the air to flow into the Zn-air battery. The anode electrode is made up of porous zinc powder which is mixed with KOH electrolyte. Air is dispersed on to the cathode electrode with the help of an air distribution membrane and air diffusion Teflon layer, as shown in Fig. 38.3. The current collector for the cathode is the carbon-pressed nickel-plated screen, which is separated from the anode material by a separator. The oxygen from the dispersed air is converted into hydroxide ions on the cathode electrode (38.33) and the hydroxide ion migrates to the

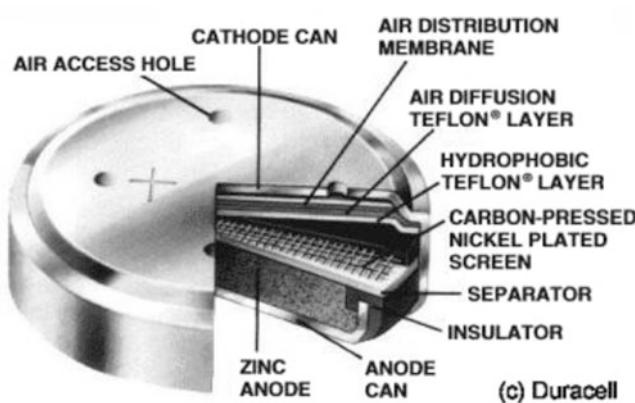


Fig. 38.3 Illustration of Zinc-air button cell [20]. The Zn-air battery has holes for air to pass through the cathode can. The oxygen present in the air is the active material for the cathode side and the Zn is the active material in the anode side. The spacing on the cathode side is smaller than any other battery

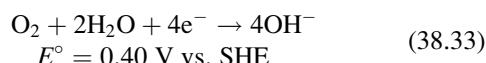
anode side to react with Zn. In this reaction, water or electrolyte is not consumed; only the Zn paste is consumed, which implies that replacement of the Zn paste could extend the operation of Zn-air batteries. A sectional view of zinc-air battery is displayed in Fig. 38.3.

The electrochemical reactions at the anode and the cathode electrodes of the Zn-air battery are listed below [33].

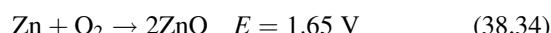
Anode reaction



Cathode reaction



Overall reaction



Theoretically, a zinc-air battery will produce 1.65 V, and it has the highest specific energy density (340 Wh/kg) of all of the primary batteries [20, 39]. The high specific energy density, flat discharge voltage, long shelf life, environmentally safe nature, and low cost of the Zn-air batteries make them attractive storage devices for many applications [20, 40]. Even though the initial application of Zn-air batteries was restricted to button cells for hearing aids, the recent developments on Zn-air batteries have found applications in cell phones, heavy equipments, and electric vehicles [41].

Zn-air batteries are limited by the amount of zinc present as active material in the anode electrode. The shelf life of the Zn-air battery will be affected by the self-discharge of the

battery, meaning the corrosion of zinc will degrade the battery capacity. Other factors affecting the capacity or shelf life of a Zn-air battery are based on the gas transfer mechanism which takes place on the cathode side. The issues associated with gas transfer mechanism are direct oxidation, carbonation of electrolyte, and effect of water vapor transfer [20]. The process of the zinc anode's being directly oxidized by the oxygen that has passed into the cathode side after diffusing through the electrolyte is known as the direct oxidation mechanism. Carbonation of the electrolyte is observed when the alkaline electrolyte reacts with the carbon dioxide present in the atmosphere, and the electrolyte transforms into metal carbonate and bicarbonate. The degradation of the Zn-air battery is caused by the formation of carbonate crystals on the cathode structure which affects cathode performance. The presence of carbonate in the electrolyte will also increase the vapor pressure and enhance the loss of water vapor. Finally, any deregulation in the transfer of water vapor between the electrolyte and the environment will significantly affect the shelf life of the Zn-air battery.

Secondary Batteries

The secondary batteries that are described in this section are the LAB, nickel-cadmium, nickel metal hydride, and Li-ion batteries. The characteristics of the selected secondary batteries are provided in Table 38.7.

Lead Acid Battery

The LAB, which is based on electrochemical principles, was first invented in 1860 by Planté. Over the years, this battery has been thoroughly studied, researched, and developed. In the category of medium to large sized batteries, the LAB is the most commonly manufactured rechargeable battery. The negative electrode for this battery is a lead paste covered grid, and the positive electrode is the plate or grid which has lead dioxide. In secondary or rechargeable batteries, an electrode which behaves as an anode during the discharge process will act as cathode during the charging process because of the reduction reactions taking place at this electrode. The electrodes are therefore referred to as negative and positive terminals instead of as anode and cathode. The grid is made of a lead-antimony alloy and the electrolyte for the LAB is sulfuric acid. The discharging and charging reactions for both the terminals are given below: [42]

Negative terminal reactions

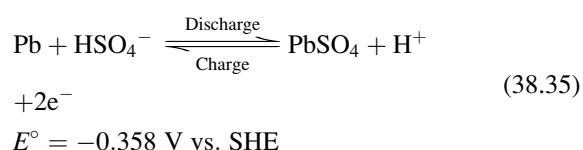


Table 38.7 Comparison of the characteristics of some secondary batteries

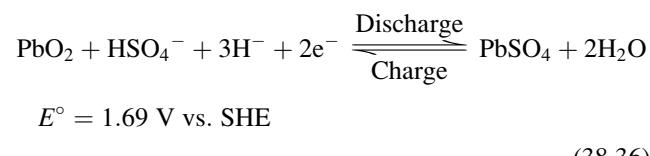
Characteristics	Lead acid (SLI design)	Nickel-cadmium (sealed design)	Nickel metal hydride	Lithium ion (C/LiCoO ₂ system)
Anode	Pb	Cd	MH	C
Cathode	PbO ₂	NiOOH	NiOOH	LiCoO ₂
Electrolyte	H ₂ SO ₄ (aqueous solution)	KOH (aqueous solution)	KOH (aqueous solution)	Organic solvent ^a
Open-circuit voltage (V)	2.1	1.29	1.4	4.2
Nominal voltage (V)	2.0	1.2	1.2	4.0
Operating voltage (V)	2.0–1.8	1.25–1.00	1.25–1.10	4.0–2.5
End voltage (V)	1.75	1.0	1.0	2.5
Operating temperature (°C)	–40 to 55	–40 to 45	–20 to 50	–20 to 55
Energy density at 20°C (Wh/kg)	35	30–35	50	90
Power density	High	Moderate to high	Moderate to high	Moderate
Self-discharge rate at 20°C (% loss per month)	2–3 ^b	15–20	20	5–10
Cycle life	200–700	300–700	300–600	500–1,000

Source: Linden [20]

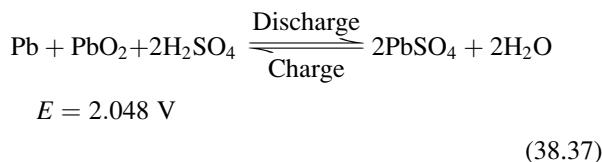
^aOrganic solvents such as propylene carbonate, ethylene carbonate, ethyl methyl carbonate, and so on

^bMaintenance-free design

Positive terminal reactions



Overall reactions



During the discharge process, the electrolyte (sulfuric acid) reacts with lead and lead dioxide to form lead sulfate and water. The cell voltage observed for an LAB is slightly more than 2V, and its specific energy density ranges between 25 and 35 Wh/kg [25]. The density of the sulfuric acid solution is often measured to estimate the status of charge for the battery. A fully charged LAB should possess 1.27–1.30 relative density for the electrolyte.

Since the LAB is a rechargeable battery, the external electricity is used to convert PbSO₄ to PbO₂ and Pb at the positive and negative terminals, respectively. This charging process also results, however, in secondary reactions, such as the evolution of oxygen at the positive terminal and the liberation of hydrogen gas at the negative terminal. These secondary reactions are the main cause for the loss of water in the electrolyte. As a result, the lead acid batteries have to be periodically replenished with water.

Research studies indicate that the presence of antimony on the lead grid electrodes was the cause for the secondary reaction which includes water electrolysis and that resulted in loss of water from the electrolyte. In order to avoid periodic replenishment of water and to retain a low maintenance LAB, the chemical composition of the electrode was changed to lead-calcium or lead-calcium-tin alloy instead of lead-antimony. The amount of water lost from the electrolyte in the low maintenance LAB is less than that lost in traditional lead acid batteries. Recent advances in lead acid batteries have focused on developing completely sealed systems. The new LAB is called a valve-regulated lead acid (VRLA) battery. In a VRLA battery, the oxygen gas generated at the positive terminal is transported internally to the negative terminal, where the oxygen is reduced with protons to form water. This process is known as the oxygen cycle [25]. The advantage of the VRLA battery is that no maintenance is required, and no gases (H₂ and O₂) escape from the battery system.

The lead acid batteries have been mainly used for automotive applications. Those batteries which are used for automotive purposes are referred to as an SLI (starting, lighting, and ignition) system. The SLI system of lead acid batteries finds application in automotive vehicles, golf carts, tractors, and lawn mowers. Additionally, the LABs are used in industrial trucks and electric vehicles for traction or motive power. The VRLA battery has been used for stationary applications, such as emergency and standby power systems, telecommunications, uninterrupted power supply (UPS), railroad signaling, and energy storage systems. The advancement in the LAB research has lead to portable systems which are sealed and maintenance-free systems. The portable lead acid batteries are mainly used in small

appliances and devices, portable tools, and electronic equipments [20].

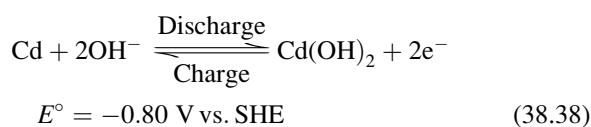
The generation of hydrogen and oxygen gas during the operation of the LAB limits its shelf life and capacity. These gases are released at levels which can lead to explosions, as in the case of SLI type lead acid batteries. Even in the sealed lead acid batteries, certain amounts of hydrogen gas are released during its operation; therefore, care must be taken while planning for charging and location of the battery for safety reasons. The lead acid batteries fail mostly due to the corrosion of the positive and negative grids or terminal. Lead and lead oxide, the active materials in negative and positive terminals, respectively, will react with sulfuric acid even if the battery is in idle condition. Therefore, grid corrosion is a major problem for the failure of lead acid batteries [20].

Nickel-Cadmium

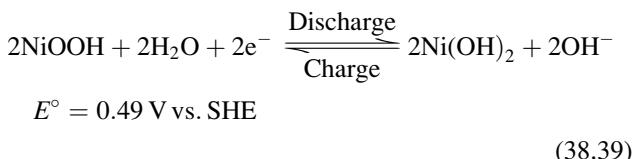
The nickel-cadmium (Ni-Cd) battery is one of the rechargeable alkaline batteries because it uses KOH as its electrolyte. Ni-Cd battery was invented in the early twentieth century by the Swedish scientist Waldemar Jüngner. Almost at the same time, Thomas Edison in the USA invented another kind of nickel-based battery known as the nickel-iron battery, which also had similar electrochemical properties to those of the Ni-Cd battery [42, 43].

The negative terminal of an Ni-Cd battery has cadmium as the active material, whereas nickel oxyhydroxide (NiOOH) is the active material in the positive terminal. During the discharge process, cadmium, in the negative terminal, is oxidized by the hydroxide ion present in the electrolyte to form cadmium hydroxide. Nickel oxyhydroxide, in the positive terminal, is converted into nickel hydroxide. During the charging process, cadmium hydroxide is reduced to metallic cadmium at the negative terminal, and Ni^{2+} in the nickel hydroxide is converted into the Ni^{3+} species as nickel oxyhydroxide at the positive terminal [44, 45].

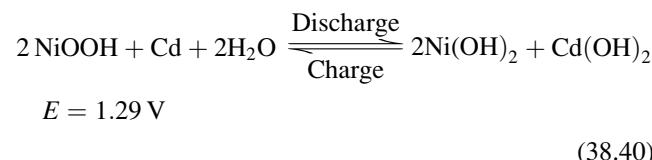
Negative terminal reactions



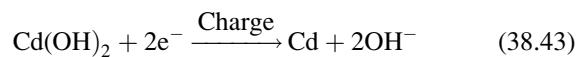
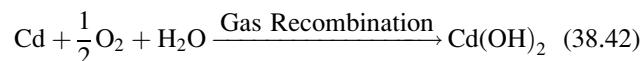
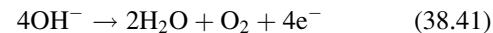
Positive terminal reactions



Overall reactions



Thermodynamically, the cell voltage for the Ni-Cd battery is 1.30 V. However, in practice, the voltage output is 1.20 V. Over the years, the specific energy density for Ni-Cd has improved from 30 to 40 Wh/kg to 60 Wh/kg [42]. Overcharging of the Ni-Cd battery will produce oxygen gas on the positive terminal (38.41). Since the positive terminal always gets fully charged before the negative terminal charges, generation of oxygen gas is a frequent occurrence at the positive terminal. Oxygen formed at the positive terminal will be transferred to the negative terminal with the help of oxygen permeable separator, for recombination with Cd to form cadmium hydroxide (38.42) [45]. Finally, the cadmium hydroxide will be converted into metallic cadmium during the overcharging process (38.43) [29]. These reactions are similar to the oxygen cycle found in the low maintenance and VRLA batteries.



Sealed Ni-Cd battery was developed to avoid gassing (oxygen) from the positive terminal. Until nickel-metal hydride batteries came along in 1991, the Ni-Cd batteries were the main choice as the power supply for all cordless or portable electronic equipment [44]. The longer cycle life of the Ni-Cd battery has resulted in its extensive use in the spacecraft applications, such as satellites in low earth orbit (LEO) and geo-synchronous earth orbit (GEO) [45].

The limitations of using the Ni-Cd batteries have been associated with the generation of gases on the electrodes during the charge-discharge process. The operation of the Ni-Cd batteries is affected by the generation of hydrogen gas on the positive terminal due to over discharging. Even in a sealed Ni-Cd battery, the evolved hydrogen gas is consumed at a low rate, which leads to a buildup of internal pressure and eventually bursting of the Ni-Cd battery [45]. At the same time, during the charging process of a sealed Ni-Cd battery, the water formed at the positive terminal will dilute the electrolyte concentration on the pores of the active material, thereby causing a drop in electrode voltage or

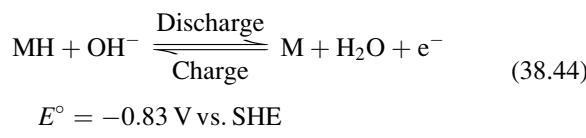
overvoltage. While operating the Ni-Cd battery in a low temperature environment with high rate of charging and discharging, the formation of water at the pores of the positive terminal will lead to the dilution of the electrolyte and freezing. However, on the negative terminal the electrolyte concentration will increase resulting in precipitations on the pores [45]. In addition to these issues, the Ni-Cd battery has the inherent problem of using a carcinogenic material, cadmium, which is also a pollutant that will harm the environment.

Nickel Metal Hydride

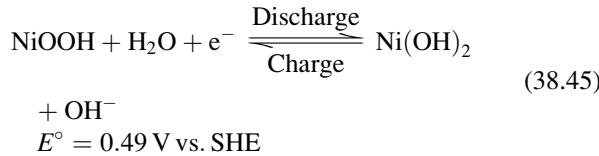
The Ni-MH battery is similar to the nickel-cadmium battery in most aspects, except for the active material in the negative terminal. The active material in the negative terminal is hydrogen, which is stored in the form of metal hydride. The hydrogen atoms are stored in metal alloys and these alloys are of two kinds, AB_5 -type and AB_2 -type. The AB_5 -type alloy is made up of nickel and rare earth metals, whereas the AB_2 -type alloy is a mixture of nickel, titanium, vanadium, and zirconium [45]. Typically, the negative terminal electrode is made of either $LaNi_5$ (AB_5 -type) or $TiNi_2$ (AB_2 -type) alloy and the AB_5 -type alloys have better corrosion resistance than the AB_2 -type [25]. In recent commercial development of the Ni-MH battery, the alloy composition for the negative electrode has been $MmNi_{3.2}Co_{1.0}Mn_{0.6}Al_{0.11}Mo_{0.9}$ (AB_5 -type) or $Ti_{0.51}Zr_{0.49}V_{0.70}Ni_{1.18}Cr_{0.12}$ (AB_2 -type), where Mm is misch-metal, which is composed of 25 wt. % La, 50 wt. % Ce, 7 wt. % Pr, and 18 wt. % Nd [45].

$NiOOH$ is the active material for the positive terminal and the aqueous KOH is the electrolyte. The reactions at the terminals are listed below: [33]

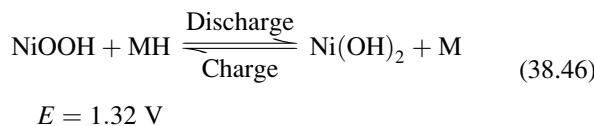
Negative terminal reactions



Positive terminal reactions

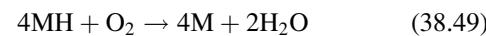
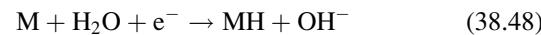
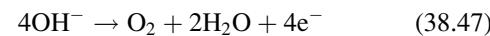


Overall reactions

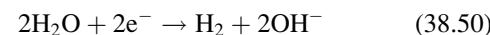


The Ni-MH battery has been replacing the Ni-Cd battery in various types of electronic equipment because the specific energy density of the Ni-MH battery is 60–80 Wh/kg, which is higher than that of the Ni-Cd battery. The cell voltage of the Ni-MH battery is similar to that of the Ni-Cd battery, ranging between 1.2 and 1.3 V.

One of the advantages of using the Ni-MH battery over the Ni-Cd battery is the absence of a toxic pollutant (cadmium) in the battery system. The evolution of hydrogen and oxygen gases, even in the sealed Ni-MH battery during overcharging and discharging conditions, has been effectively eliminated by the design of the battery [45]. During the overcharging step, oxygen gas is produced at the positive terminal; the oxygen gas then migrates to the negative terminal, where it reacts with metal hydride electrode to form water (38.47), (38.48), and (38.49):



Similarly, during the deep discharging process, hydrogen gas is evolved from the positive terminal (38.50). The hydrogen gas migrates to the negative terminal, where it is oxidized into water in the presence of the metal hydride electrode (38.51).



The Ni-MH batteries do not show any memory effect caused by recrystallization on the electrodes. Moreover, the Ni-MH batteries have higher energy density in terms of weight and volume in comparison with the Ni-Cd batteries, which has resulted in the replacement of the Ni-Cd batteries by the high energy density Ni-MH batteries. In addition to the application of the Ni-MH batteries for all of the electronic devices, the prismatic cells with 250 Ah capacity are manufactured for electric vehicle applications. The Ni-MH batteries are capable of operating only in the temperature range of -20 to $+45^\circ\text{C}$; beyond 45°C , the charging efficiency of the battery has been observed to decline [45].

The swelling of the electrode material from absorption of hydrogen gas and the leaching of the metal ions present in the electrode into the electrolyte are some of the issues related to Ni-MH batteries. The hydrogen storage materials have the problem of severe volume expansion with more intake of hydrogen gas. This excessive absorption of hydrogen gas can occur from the charging—discharging process, and the absorption of hydrogen gas can lead to cracking and

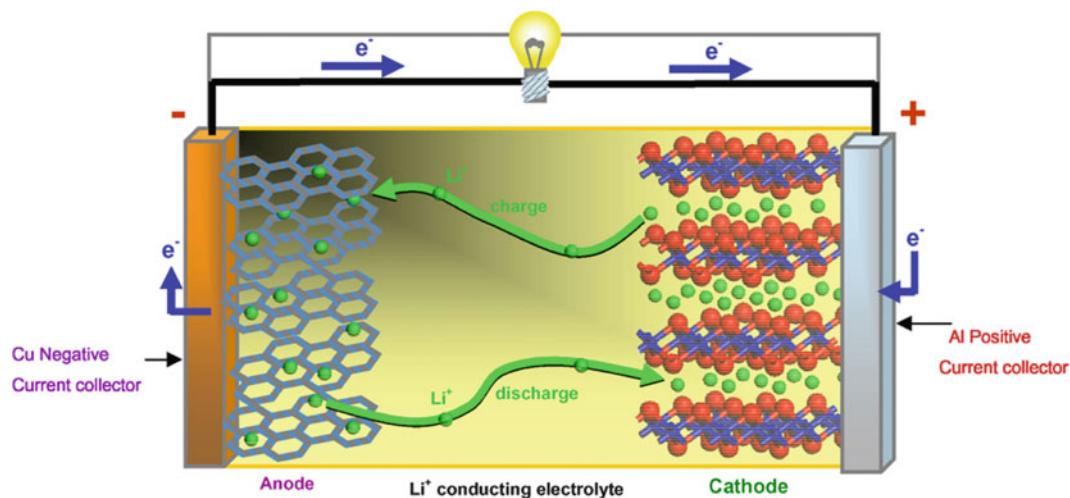


Fig. 38.4 Illustration of discharge and charge processes of Li-ion battery [46]. Copper is the negative current collector and it has graphite on the surface. Aluminum is the positive terminal with LiCoO_2

compound on the surface. The intercalation of Li-ions during charging and discharging is shown in this figure

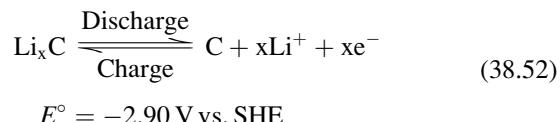
pulverization of alloy present in the electrode [45]. The leaching of the metal ions from the metal alloy electrodes, due to the presence of organic impurities in the electrolyte, will lead to self-discharge of the battery and eventual decay of the battery capacity. The separators used in the Ni-MH battery can also decompose and disperse the organic impurities in the electrolyte, which is another problem related to Ni-MH batteries.

Lithium Ion Battery

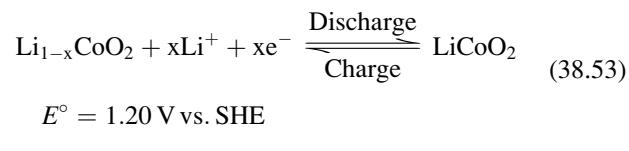
Lithium is the lightest element among all the materials used in batteries. The standard reduction potential for Li is -3.04 V vs. SHE, which makes it a suitable component for batteries. Lithium batteries, commonly used in cameras, have an average cell voltage of 3.5 V. Lately, however, another kind of lithium battery, the lithium ion battery (LIB), has demonstrated higher cell voltages in the range of 4 V and a specific energy density of $100\text{--}150$ Wh/kg, which translates into a longer cycle life than any other commercial battery [27]. So, the LIB finds application in mobile phones, laptops, portable music players, and even as a power supply unit for electric vehicles [43].

The electrochemistry for the LIB is not substantially different from other batteries. Graphite is the active material in the negative terminal and the positive terminal is made of lithium metal oxide compounds, such as LiCoO_2 and LiNiO_2 . The element lithium is highly reactive and can catch fire, or even explode, when it comes in contact with water. So, the electrolyte used in the LIB is a nonaqueous solution, such as a combination of lithium salt (LiPF_6) with organic solvents, namely ethylene carbonate-dimethyl carbonate (EC-DMC). The electrochemical reactions for the LIB with LiCoO_2 as the active material in the positive terminal are listed below: [33]

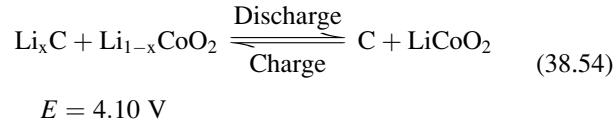
Negative terminal reactions



Positive terminal reactions

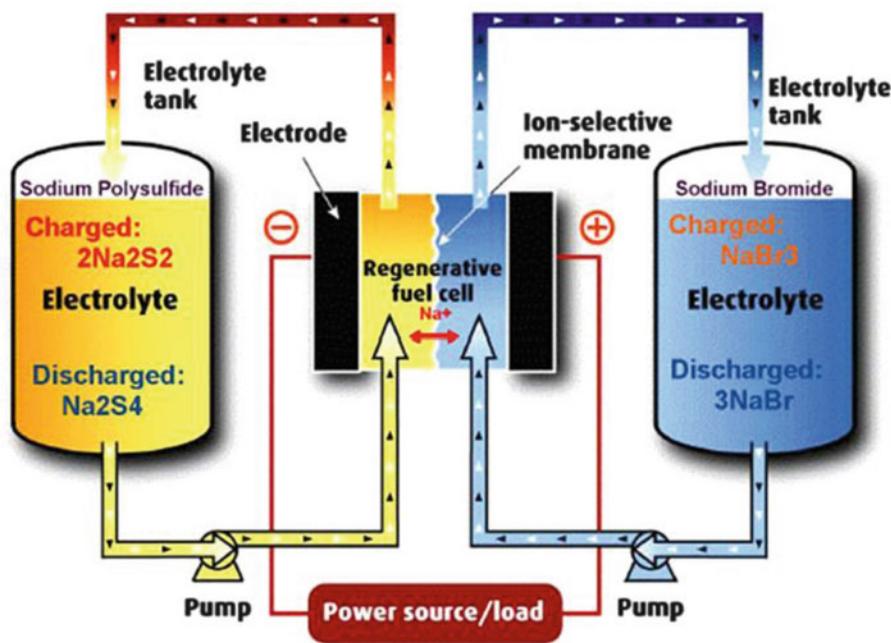


Overall reactions



During the charging process, the Li-ions present inside the structures of the LiCoO_2 compound are removed or withdrawn, and transported via the mixed organic electrolyte into the graphite structure of the negative terminal. This process is reversed during the battery discharge by removing Li-ions from the graphite structure, and it is intercalated into the LiCoO_2 structure. The phenomena of Li-ion transported back and forth between anode and cathode material has led to the naming of the Li-ion battery as a “rocking-chair” cell [42]. The current collector used for the anode or the negative terminal (graphite) is copper, and aluminum is the current collector on the cathode or the positive terminal side (Fig. 38.4).

Fig. 38.5 Schematic diagram of polysulfide bromide battery (flow battery) [24]. The flow battery shown in this figure has reservoirs containing charged and discharged species of the compounds for each terminal. Sodium polysulfide solution is circulated on the negative side and sodium bromide is circulated through the positive side of the flow battery



Many researchers are working to improve and develop better Li-ion batteries for various applications. Electrolytes used in the first generation of Li-ion batteries have been liquid organic solvents, but the use of polymer and ceramic electrolytes has simplified the battery design resulting in improved safety and durability [46, 47]. Polymer electrolytes being studied are PEO, a solid polymer electrolyte, and poly(vinylidene fluoride) (PVdF) with hexafluoropropylene (HFP), a polymer gel electrolyte. In the case of ceramic electrolytes, $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$, or LAGP, is considered to have relatively high conductivities [47]. In the same manner, different electrode materials for the LIB are being investigated as well. Anode materials that have caught the researcher's attention are carbon nanotubes (CNTs) with alloys, such as Sn_2Sb and SnNi , and Li alloys, such as LiAl , Li_3Sb , Li_2Si_5 , and Li_2Sn_5 [46, 48]. In the case of cathode materials for the Li-ion batteries, LiMn_2O_4 , vanadium oxides (V_2O_5), olivines (LiFePO_4), and layered lithium metal oxides— LiMO_2 ($\text{M} = \text{Mn, Ni, Co}$) have been actively considered [46, 48].

Flow Batteries

Other than the primary and secondary batteries, there are new types of batteries, which constitute the emerging technologies in the field of battery, also being investigated. The research activity surrounding these new types of batteries are focused mainly to improve the energy density of the battery system and also to develop advanced energy storage device capabilities. Among the new kinds of

batteries, redox flow and high temperature batteries have demonstrated promising future.

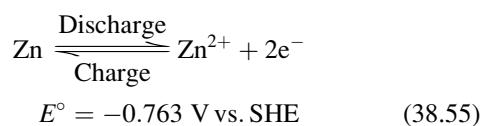
The redox flow batteries are suited as energy storage units for the distributed power supply installations. The outlook for using the redox flow batteries is in stand-alone power applications and distributed energy installations for electric utility service. The salient features of the redox flow batteries are its modular design, ease in transportability, low cost compared to other power generation systems, long life, and high reliability [26]. A few examples of the redox flow battery systems are polysulfide-bromide, zinc-bromine, and vanadium-bromide redox flow cells [24, 49]. Recent advances and further reading on the flow batteries can be found in the literature [50–59].

The design and structure of a redox flow battery, as shown in Fig. 38.5, resemble a fuel cell rather than the traditional rechargeable battery. The functioning of the redox flow battery, however, is different from that of a fuel cell. A simple diagram of the polysulfide bromide flow battery is shown in Fig. 38.5. The positive and negative compartment of the redox flow cell is separated by an ion-selective membrane which provides the ionic conductivity required for the electrochemical reactions at the electrodes. The electroactive species for the positive and negative sides are dissolved in their respective electrolyte solutions. The electrolyte tank for the negative side of the polysulfide bromide battery has both disodium disulfide (Na_2S_2) and disodium tetrathionate (Na_2S_4), which are the charged and discharged compounds, respectively. Similarly on the positive side, the electrolyte has sodium tribromide (NaBr_3) as the charged species and sodium bromide (NaBr) as the

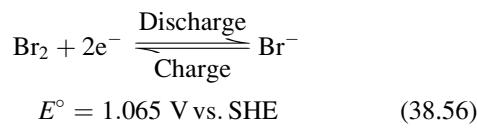
discharged species. The presence of charged and discharged species in an electrolyte is not used in the fuel cell system. These electrolyte solutions are circulated into their respective negative or positive side of the flow cell so that the electroactive species will be reduced or oxidized, and produce the electric voltage. The energy of the redox flow battery system depends on the volume of the electrolyte tank, so the energy component of this battery is determined independently from the battery power, which is based on the flow cell.

The electrochemical reactions for the $ZnBr_2$ system are listed below, where bromine gas combined with organic reagent forms polybromide compound in the positive electrode. The thermodynamic cell voltage for the $ZnBr_2$ system is 1.83 V, but only 1.3 V is typically observed during its operation [43].

Negative terminal reactions

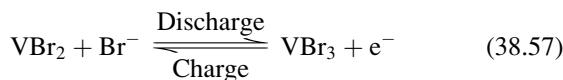


Positive terminal reactions

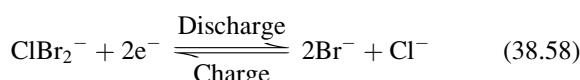


Another flow battery is based on the vanadium-bromide redox system. Normally, the specific energy density for the vanadium-bromide redox flow battery, for an ion concentration of 2 mol/L, is 25–35 Wh/kg. When the ion concentration of the redox species is increased to 3–4 mol/L, the specific energy density of the flow battery also increases to 60 Wh/kg. The negative electrode of this redox flow battery is the VBr_2/VBr_3 redox couple and the $Cl^-/ClBr_2^-$ redox couple is present at the positive electrode [26]. The reactions for the vanadium-bromine redox flow battery are as follows:

Negative terminal reactions



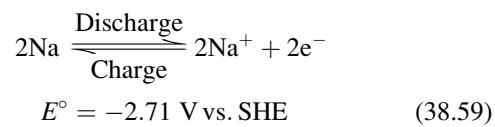
Positive terminal reactions



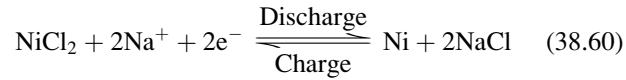
High Temperature Batteries

New types of batteries, such as sodium (Na) beta batteries (NBBs), utilize high temperatures for their effective functioning. These NBBs have beta alumina as their solid electrolyte, in order to handle high temperatures. One of the beta batteries is the sodium-nickel chloride battery, also known as ZEBRA (ZEelite Battery Research Africa), so named because it was first developed in South Africa. The active material in the anode, or the negative terminal, for the ZEBRA battery is molten Na. The active material at the positive terminal is nickel chloride. The primary electrolyte used to separate anode and cathode is β'' -alumina. In addition to β'' - Al_2O_3 , the battery also has a secondary electrolyte in the form of molten sodium aluminum chloride ($NaAlCl_4$), which provides good mobility for sodium ions. The sodium-nickel chloride battery is operated between 175 and 400°C. The electrochemical reactions at the electrodes are as follows: [49]

Anode, or negative, terminal reactions



Cathode, or positive, terminal reactions



Overall reactions

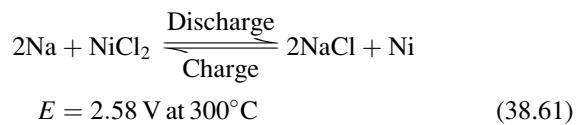


Figure 38.6 displays a schematic diagram of the sodium-nickel chloride battery. In this battery, liquid sodium is enclosed in a metal shim and held in an anode end plate. The anode or the negative terminal side is separated from the cathode or the positive terminal side by copper wool. The copper wool separator comes in contact with the solid electrolyte (β'' -alumina). In the cathode, which is the positive terminal side, the current collector is an Ni mesh which is surrounded by the active material for the cathode— $NaAlCl_4$. The α -alumina ring is the secondary electrolyte of the sodium-nickel chloride battery.

The sodium beta battery technology based on the beta alumina solid electrolyte has recently attracted interest for applications such as renewable energy storage, as well as

Fig. 38.6 Schematic diagram of a Sodium-nickel chloride battery [140]. Cross-section view of the high temperature battery system, where solid electrolyte is β'' -alumina, anode is molten sodium, and molten NaAlCl_4 is the cathode material

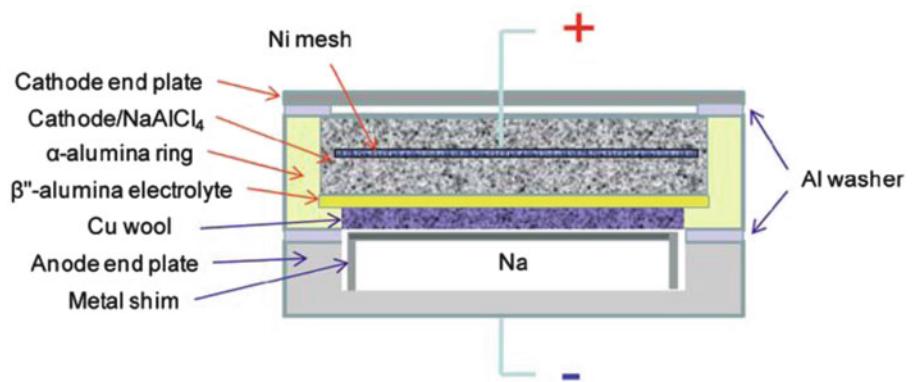
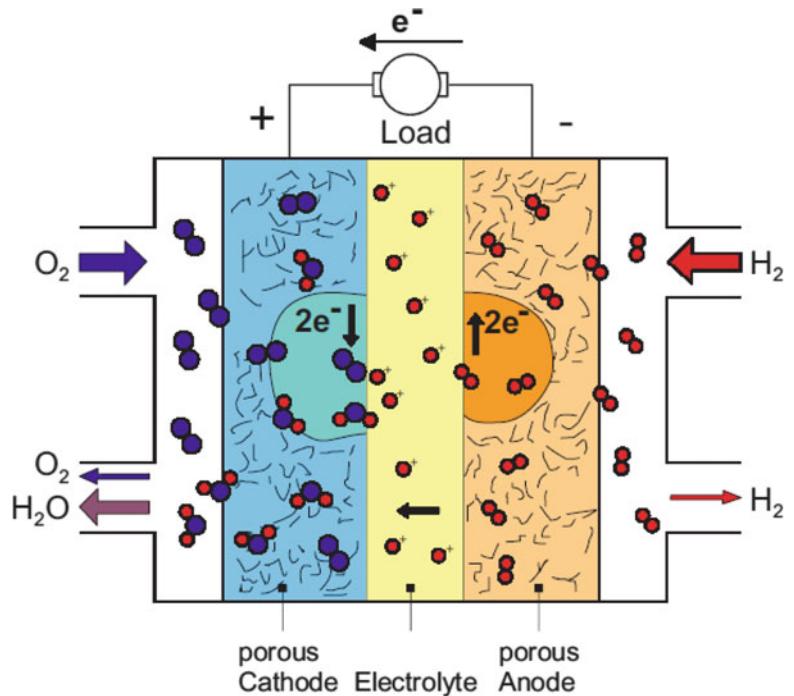


Fig. 38.7 Schematic drawing of a proton exchange membrane fuel cell (PEMFC) [31]. The electrolyte is capable of conducting or exchanging protons between anode and cathode. On the anode side H_2 is oxidized to protons on Pt surface over the porous anode. In the cathode side, the proton combines with O_2 to form water which is removed along with unreacted O_2



electric vehicles, because of its high energy density, high round-trip efficiency, and capacity to store energy for long durations [49].

Fuel Cells

In 1839, Sir William Grove invented an electrical energy conversion system known as fuel cells. The fuel cell is an electrochemical device which can directly convert chemical energy bound up in a chemical compound into electrical energy. Figure 38.7 is the schematic diagram of a proton exchange membrane fuel cell (PEMFC). Similar to the battery system, the fuel cell has anode and cathode compartments. The electrolyte used in the PEMFC is solid polymer electrolyte, Nafion (sulfonated tetrafluoroethylene-based fluoropolymer-copolymer). Hydrogen gas (the fuel) is

supplied to the anode side of the fuel cell, and the cathode side needs oxygen or the oxygen present in the air for the electrochemical reaction. The reactants supplied to the fuel cell are in gaseous form. Both the anode and cathode side have a porous electrode with platinum (Pt) as the catalyst for the electrochemical reactions. On the anode side, hydrogen gas is oxidized to become a proton, which travels through the solid electrolyte to the cathode side. On the cathode side, the proton, along with electrons from an external circuit, reacts with oxygen to form water and produce an electric current.

According to Fig. 38.7, the hydrogen gas is fed to the anode side of the PEMFC and the platinum catalyst on the porous anode oxidizes a hydrogen molecule into a proton and two electrons (38.62). The electrons travel through the external circuit and the protons are transported through the proton exchange membrane (PEM), or the electrolyte, to the cathode side. On the cathode side, the protons combine

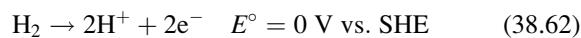
Table 38.8 Characteristics of the different types of fuel cells

Characteristics	AFC: alkaline fuel cell	PEMFC: proton exchange membrane fuel cell	DMFC: direct methanol fuel cell	PAFC: phosphoric acid fuel cell	MCFC: molten carbonate fuel cell	SOFC: solid oxide fuel cell
Electrolyte	Potassium hydroxide (8–12 N)	Proton exchange membrane	Proton exchange membrane	Phosphoric acid (85–100 %)	Molten carbonate (Li, K, Na)	Solid oxide ($\text{ZrO}_2\text{-Y}_2\text{O}_3$)
Operating temperature	50–250°C	50–90°C	50–90°C ($\leq 130^\circ\text{C}$)	180–200°C	650°C	750–1,050°C
Charge carrier	OH^-	H^+	H^+	H^+	CO_3^{2-}	O^{2-}
Electrocatalyst	Pt, Ni/NiO_x	Pt	Pt	Pt	Ni/LiNiO_x	Ni/Perovskites
Fuel	H_2	H_2 (pure or reformed)	CH_3OH	H_2 (reformed)	H_2 and CO (reformed), CH_4	H_2 and CO (reformed), CH_4
Poisons	CO, CO_2	$\text{CO} > 10 \text{ ppm}$	Adsorbed intermediates	$\text{CO} > 1 \%$ $\text{H}_2\text{S} > 50 \text{ ppm}$	$\text{H}_2\text{S} > 0.5 \text{ ppm}$	$\text{H}_2\text{S} > 1 \text{ ppm}$
Applications	Transportation, space, military, energy storage systems			Combine heat and power for decentralized stationary power systems	Combined heat and power for stationary decentralized systems and for transportation (trains, boats, etc.)	
Realized power	Small plants 5–150 kW Modular	Small plants 5–250 kW Modular	Small plants 5 kW	Small–medium plants 50 kW–11 MW	Small power plants 100 kW–2 MW	Small power plants 100–250 kW

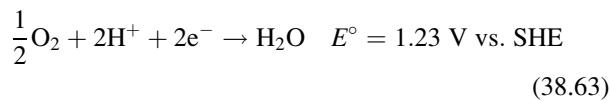
Sources: Srinivasan et al [32]; Carrette et al [31].

with the electrons and the oxygen gas on the porous cathode in the presence of Pt catalyst to form water (38.63) and produce an electric current. The oxygen gas stream is supplied to the cathode side and the water produced from the electrochemical reaction is carried away by the exiting oxygen stream. The electrochemical reactions at the anode and the cathode electrodes of the PEMFC are listed below.

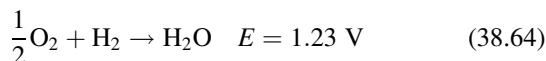
Anode reaction



Cathode reaction



Overall reaction



Fuel cells are capable of generating power as long as the fuel (hydrogen) and the oxidant (oxygen) are supplied to the system. On the other hand, even a rechargeable battery is limited in generating power; as all secondary batteries have a definite number of rechargeable cycles, known as cycle life, a rechargeable battery can be recharged (see Table 38.7). In

the case of the redox flow battery, the charged and discharged species of the electrochemical reaction are stored in the electrolyte. There are two different electrolytes, one for the anode and one for the cathode. Conversely, the fuel cell has a single electrolyte with the ability to conduct ions between the anode and the cathode. The fuel cell is not designed to be recharged like in the secondary batteries to extend the battery life. A list of different types of fuel cell and its characteristics has been complied in the following Table 38.8.

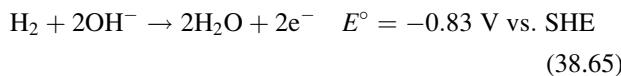
Notice that traditionally the names for the fuel cells were based on the type of the electrolyte used in that system, except for the Direct Methanol Fuel Cell (DMFC). The DMFC is a PEMFC which uses methanol as its fuel. The most significant problems with adopting fuel cell technologies have to do with: hydrogen storage, transportation, and production. Alternative solutions for these problems will be discussed later in the chapter (see section on “Trends: Novel Electrosynthesis Processes”).

Alkaline Fuel Cell

The alkaline fuel cell (AFC) has the highest electrical efficiency (>60%) among all the types of fuel cells. In the USA, the National Aeronautics and Space Administration (NASA) has used the AFC power plant in the Apollo missions and Space Shuttle program due to its higher efficiency and proven reliability. Initially, nickel-based catalysts were used in the AFCs before switching to a Pt electrocatalyst.

However, one of the advantages of the AFC is that it can employ other metals as the catalyst, such as Pt-Co alloy for oxygen reduction reactions [60]. At the beginning, the AFCs used in the Apollo missions were operated at 200–230°C, whereas now the AFCs are normally operated less than 100°C. The electrochemical reactions at the anode and the cathode electrodes of the AFC are given below:

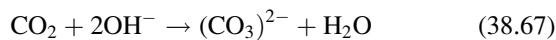
Anode reaction



Cathode reaction



The alkaline electrolyte provides better ionic conductivity than acid electrolytes for the fuel cell [32]. Additionally, the fuel cells with alkaline electrolyte, such as KOH used in the AFC, has displayed better kinetics for the oxygen reduction reaction compared to the acid electrolytes [31]. In space applications, the KOH electrolyte for the AFCs is stabilized in an asbestos matrix, which has provided limited life for the fuel cell. In 1970, researchers found that circulating the KOH electrolyte increased the life of the AFC. Carbon dioxide (CO₂) found in the atmosphere and the alkaline electrolyte have been found to be detrimental to the operation of the AFC. CO₂ will react with the hydroxyl ion (OH⁻) to form carbonate, which would precipitate on the electrode and the electrolyte, thereby decreasing the performance of the AFC (38.67). In this manner, electrolyte circulation will help in removing the CO₂ gas and reduce the build-up of carbonate in the electrolyte, which extends the life of the AFC. Additionally, a CO₂ scrubber can be used for the hydrogen and air streams in order to reduce the amount of CO₂ in the fuel cell.



The AFCs have been used in Apollo space craft and other shuttle programs by NASA. Both the USA and Russia have extensively used the AFCs in their space flights [32]. In addition to the space industry, the highly efficient fuel cell (AFC) also found application in the transportation sector. In 1970s, Kordes built the first fuel cell car using the AFC. In one of the projects, the London cabs were fitted with AFCs modules to provide up to 10 kW power. The cab also had a battery to start and operate the car for the first 10 min before the fuel cell could generate enough power to control the vehicle [31]. Energy storage was the other application of

the AFCs. Around the world various organizations, such as Allis-Chalmers, Siemens, Union Carbide, Exxon/Asthom, Fuji, Varta, IFP, CGE, and ELENCO, have installed and tested 1–10 kW capacity of AFC systems [32].

Proton Exchange Membrane Fuel Cell

The PEMFC was formerly known as solid polymer electrolyte membrane fuel cell. These fuel cells use polymer electrolyte as a membrane, which is capable of transporting protons between the anode and the cathode side. The membrane used in these fuel cells is Nafion, which is a perfluorocarbon sulfonic acid membrane. The Nafion membrane is highly acidic in nature with good conductivity for protons in the presence of water. Since Nafion structure is similar to Teflon, it is highly stable in oxidizing and reducing environments [31, 32]. Water management is very important for the efficient functioning of the PEMFC. The gas (hydrogen and oxygen, or air) streams are hydrated before being supplied to the fuel cell, so that ionic conduction of proton across the Nafion membrane can be maintained.

The operating temperature for the PEMFC is in the range of 50–90°C. Pt is the catalyst used in both the anode and cathode electrodes. The electrodes are made of porous gas diffusion electrodes (GDE) so that the gases can have better contact with the Pt catalyst. The electrodes for the PEMFC are prepared in a delicate manner in order to obtain the least resistance between anode, electrolyte, and cathode. This method to combine Pt, catalyst support, binders, and the Nafion membrane is known as membrane electrode assembly (MEA). Dispersion of Pt on carbon support enhances the oxygen reduction reaction on the cathode electrode. If air was used in the cathode side of the fuel cell, then the lower partial pressure of oxygen in the air will decrease the performance of the fuel cell.

In the anode electrode, Pt is the best catalyst for oxidizing pure hydrogen gas. However, the presence of carbon monoxide (CO) in the hydrogen stream will have damaging effect on the electrode and also the PEMFC. Carbon monoxide (CO) will adhere to Pt and block the active sites from the desired electrochemical reaction, evidencing the fact that CO is the major poison for the PEMFC. Cleaning the hydrogen stream off of the CO is one of the ways to avoid CO contamination for the PEMFC. Research on developing CO tolerant catalysts, such as Pt-Ru, is also being investigated [61–65].

Even though the PEMFCs are famously known for its application in cars or for transportation, it has also been used in the Gemini spacecraft. The PEMFC provided a power of 1 kW to the spacecraft [31]. Some of the well-known companies involved in the production of PEMFCs are Ballard Power Systems, Inc. in Canada; IFC, Energy Partners, General Motors, Plug Power, and H-Power is United States; Toyota, Honda, Mazda, and Fuji in Japan;

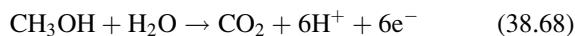
Daimler Chrysler in association with Ballard Power Systems, Inc. in Germany; and DeNora in Italy [32]. The PEMFCs are used in the modern electric vehicles to avoid the usage of gasoline in the cars. The hybrid electric vehicles are powered by batteries and fuel cells are used to sustain the power demand. Presently, most of the big car companies are involved in the development of fuel cell-based cars. For sometime fleets of PEMFC-powered buses have been operated and tested by Chicago Transit Authority and BC (British Columbia) Transit, for public transportation, with the help from Daimler Chrysler/Ballard [32].

In the area of low level power generation, the PEMFC systems are increasingly finding a good fit. Especially in the portable power applications, the PEMFCs with 35–250 W power have found use in video cameras, electric wheelchairs, laptops, intelligent transportation systems, and military communications [32]. On the other hand, the PEMFC systems are also crossing into the stationary applications. Interestingly, Plug Power has installed a 7 kW residential power system based on the PEMFCs to provide a single home in upstate New York with electricity, heat, and hot water [31].

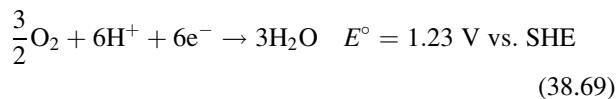
Direct Methanol Fuel Cell

The PEM technology has been used in another kind of fuel cell known as the DMFC. The DMFC operates in the same temperature range as the PEMFC, and it also transports protons across the membrane to produce water and generate electric current. There are several advantages of the DMFC over the PEMFC. One of them is that methanol can be more efficiently stored than hydrogen. Therefore, operating directly with methanol minimizes a significant problem for fuel cell technology: hydrogen storage. Additionally, the use of 1 M methanol directly in the fuel cell helps the water and thermal management of the fuel cell with the PEM. The PEM requires water for the conductivity of protons. However, at the operating temperature, the membrane dries up and the presence of liquid methanol helps in hydrating the PEM. The electrochemical reactions on the anode and cathode electrode of the DMFC are listed below:

Anode reaction



Cathode reaction



At the anode electrode, the methanol is oxidized to CO_2 , protons, and electrons. The electrons are transported through the external circuit and the protons are migrated through the

membrane to the cathode side. At the cathode electrode, oxygen reacts with the protons and the electrons to form water. Pt is not an efficient catalyst for the electrochemical oxidation of methanol, so other metals, as alloys of Pt, are investigated as possible candidates for the anode electrode of the DMFC. The most commonly used catalyst for the methanol oxidation at the anode electrode is Pt-Ru. In the cathode electrode, similar to the PEMFC, Pt is the best catalyst for the oxygen reduction reaction.

One of the issues with the DMFC system is methanol crossover, where methanol migrates through the membrane from the anode to the cathode side of the fuel cell. The membranes used in the DMFC systems were mainly developed for the PEMFC, which was designed to transport protons along with water molecules. Methanol has similar properties to the water which results in easy diffusion as well as electroosmotic drag of the methanol molecules across the PEM. The oxidation reaction of methanol at the Pt catalyst surface interferes with the oxygen reduction reaction and degrades the performance of the DMFC. Membrane development to prevent methanol crossover is the key area of research for the DMFC systems. At the same time, investigation has also been focused on a methanol resistant catalyst for the cathode electrodes. This is a different approach to solve the presence of methanol on the cathode side of the DMFC. In this approach, the methanol crossover across the membrane is not prevented but methanol tolerant catalysts are used to avoid methanol oxidation at the cathode [66–69].

The DMFCs are typically PEMFCs, which uses easily transportable liquid methanol as fuel. Similar to PEMFCs, the DMFCs have the strong potential to be used for the portable power systems. The use of methanol in these fuel cells, which has low noise and thermal signature, shows the possibility in military and defense applications for the DMFC systems. Presently, the potential applications for the DMFCs are focused on the portable power systems and military, and later it could be extended to stationary power generation.

Phosphoric Acid Fuel Cell

One of the most commercialized fuel cells is the phosphoric acid fuel cell (PAFC). The PAFC systems are used as stationary power plants. They have been installed worldwide in the range of 5–10 MW capacity. Phosphoric acid is an excellent acid electrolyte for the fuel cell system and the PAFC electrolyte, phosphoric acid, is stabilized in an SiC matrix. The hydrogen gas obtained from steam reforming or other reformation process can be handled efficiently by the phosphoric acid electrolyte [32]. The PAFCs operating temperature is around 200°C, which is suitable for the electrolyte to provide good ionic conductivity.

The phosphoric acid electrolyte is inert and stable in a reducing and oxidizing environment. The electrolyte also

has low volatility in the operating temperature. Among other advantages, the PAFC system has a relatively simple design construction, and it is also a thermally, chemically, and electrochemically stable system [31]. The high temperature operation of the PAFC has resulted in tolerances of up to 1% CO and 40 ppm H₂S. The electrochemical reactions in the anode and cathode electrodes are same as the ones observed in the PEMFCs (38.62) and (38.63). The electrocatalyst used on the anode electrode of the PAFC is Pt, whereas Pt-Co and Pt-Cr-Co supported on carbon has been studied as catalysts for the oxygen reduction reaction on the cathode electrode [32]. The expensive manufacturing cost for the PAFC systems is the main drawback from being widespread installations. The cost of the power from the PAFC power plant is still more than \$4,000/kW.

The PAFC systems are mainly applied for stationary power generation. Since the PAFC systems operate at 200°C, the heat energy from the PAFC systems is recovered by integrating it with combined heat and power (CHP) plant. The major company involved in the manufacturing of the PAFC power plants is United Technologies Corporation (UTC). UTC along with its subsidiaries has installed more than 75 MW of PAFC power plants over 19 countries. UTC has manufactured and installed at least 250 PAFC units of each 200 kW power capacity. Presently, one of the UTC's subdivision, UTC Power, Inc., is marketing 400 kW units under the name of PureCell400. A 250 kW PAFC power plant has been used to power the police station at the New York City's Central Park [70]. Toshiba has installed a factory of PAFCs at Hamakawasaki works in Japan [32]. A major power plant of 11 MW capacity was commissioned by UTC along with Toshiba to provide power for Ichihara in Tokyo [31]. Military application of the PAFC systems is being investigated by the US Army Engineering Research and Development Center, Construction Engineering Research Laboratory (ERDC/CERL) with 30 units of 200 kW PAFCs [71].

Molten Carbonate Fuel Cell

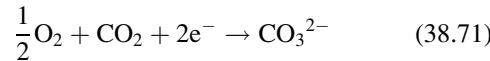
The molten carbonate fuel cell (MCFC) is one of the high temperature fuel cells. The operating temperature for the MCFC has been in the range of 600–700°C. The advantages of the MCFC systems are: the use of non-noble metal catalyst for oxygen reduction reactions at the cathode electrode due to a relatively high operating temperature; carbon dioxide is supplied as fuel and not as a poison; the waste heat generated during MCFC operation can be recovered to increase the overall efficiency of the MCFC system; and the MCFCs are capable of combining fuel reforming of natural gas in order to produce hydrogen gas for fuel cell operation [32].

The electrochemical reactions taking place on the anode and cathode electrodes are listed below:

Anode reaction



Cathode reaction



At the cathode, oxygen reacts with carbon dioxide in order to form the carbonate ion, which is the charge carrier across the electrolyte to the anode side. The carbonate ion reacts with hydrogen on the anode to form water, carbon dioxide, and electric current. Carbon dioxide is recycled back into the cathode stream.

The high operating temperature of the MCFC helps in the use of a non-noble metal catalyst, such as NiO, on the cathode electrode for oxygen reduction reaction. Alternate cathode electrodes investigated are lithium oxide based, such as LiFeO₂, Li₂MnO₃, and LiCoO₂. A double-layered catalyst like NiO/LiCoO₂ has also been used in the MCFC systems to improve the stability of the oxygen reduction reaction [72]. At the anode, Ni is used as the electrode and Ni-Al or Ni-Cr has also been used as the anode to prevent Ni creeping into the molten carbonate electrolyte.

Molten carbonate stabilized in an alumina-based matrix is the electrolyte for the MCFC. The molten carbonate is obtained from the LiCO₃/K₂CO₃ (Li/K) mixture supported on the alumina. The sodium carbonate (Li/Na) in the above mixture (Li/K) has increased the alkalinity of the electrolyte and decreased the Ni dendrite formation in the electrolyte. The issues associated with the MCFC technology include the migration of Ni from anode into the electrolyte, corrosion of the NiO at the cathode, and electrolyte migration [32].

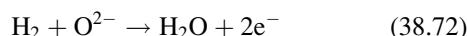
Stationary power generation is the area of focus for the MCFC technology. Among various demonstrations of this technology, the stand out and best outcome has been a 2 MW MCFC power plant at Santa Clara, California, USA. In 1996, the 2 MW MCFC power plant was built, commissioned, and tested by the Energy Research Corporation (ERC). It used natural gas as its fuel. This demonstration plant reached a maximum electrical power of 1.93 MW with 2 ppm NO_x, undetectable level of SO_x, and operated within the noise limits. In Bielefeld, Germany, a 250 kW power plant was tested by MTU Friedrichshafen, an affiliate of the Daimler Chrysler group. This power plant operated at 50% efficiency using natural gas, and it also provided heat and hot water to the university at Bielefeld. In 1997, the MC Power Corporation demonstrated a 250 kW power plant in Miramar (San Diego, USA) [31, 32].

Solid Oxide Fuel Cell

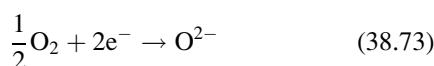
The other high temperature fuel cell is the SOFC, which utilizes solid electrolyte made of ceramic material for the

electrochemical generation of power. The SOFC operates in the range of 750–1,050°C, which is higher than the MCFC. The high operating temperature of the fuel cell helps in tolerating carbon monoxide, carbon dioxide, and, possibly, reform hydrocarbon fuels. The electrochemical reactions observed on the anode and cathode electrode of the SOFC are listed below:

Anode reaction



Cathode reaction



At the cathode electrode, the oxygen molecule from the air is oxidized to an oxide (O^{2-}) ion, which is transported through the solid oxide electrolyte to the anode side. The oxide ions combine with the hydrogen molecule on the anode electrode to form water and generate electric current. The solid oxide electrolyte commonly used in the SOFC system is made of 85–90% zirconia (ZrO_2) and 10–15% yttria (Y_2O_3), which is referred to as YSZ. The defect in the perovskite ($\text{ZrO}_2\text{-Y}_2\text{O}_3$) structure as well as the high operating temperature of the SOFC helps in the movement of the oxide ion in the solid YSZ electrolyte. The solid form of the electrolyte results in only two phases (solid–gas) being available (instead of the solid–liquid–gas phases in other types of fuel cells) for the reactions. The two phase situation eliminates the problems, such as water management, flooding of the catalyst, and slow kinetics, due to mass transport of the reactant and products in the liquid phase.

The cathode materials employed for the SOFC are lanthanide-based perovskites, especially lanthanum strontium manganate (LaSrMnO_3 —LSM). The lanthanide-based perovskites have displayed higher ionic conductivity for the oxide ion and good catalytic activity for the oxygen reduction reaction. Two phase cathode materials are investigated for the SOFC, where a layer of YSZ will be added along with LSM to form the two phase cathode. For many years, the material used as the anode for the SOFC has been Ni-YSZ. The Ni cermet is more stable than the pure Ni as the anode material for the SOFC.

The stack or planar design of the SOFC system has been well studied and documented. The most advanced design of the SOFC system has been a tubular design developed by Siemens-Westinghouse. The thermal stability of the SOFC was improved by the tubular configuration due to the presence of self-sealing structures. Incorporation of good sealing material for the SOFC system has been one of the many challenges faced by the SOFC technology. Additionally, the development of an efficient solid electrolyte, anode, and cathode material for the SOFC has always been emphasized.

Similar to the MCFC systems, application for the SOFC technology is in the stationary power generation or distributed power systems. Siemens-Westinghouse is pioneer in the field of SOFC technology. A 25 kW SOFC unit was installed by Siemens-Westinghouse and tested using natural gas at the University of California's National Fuel Cell Research Center situated in Irvine, California [32]. In 1998, Siemens-Westinghouse collaborated with NUON and ELSAM to develop a 100 kW power production plant in Westvoort, Netherlands. This power plant was able to produce 54 kW of heat from the system at normal operation conditions (400 V). This SOFC power plant has been providing electric current to the grid and hot water to the local heating system [31]. Siemens-Westinghouse has also investigated combining the SOFC systems with gas turbine to increase the overall electrical efficiency. In 1999, Siemens-Westinghouse built a 250 kW prototype of the SOFC gas turbine hybrid power plant. This hybrid power plant was tested by Edison Technology Systems at National Fuel Cell Research Center in Irvine, California [32].

Fuel Processing

The gas streams required for the fuel cells are hydrogen and oxygen, as oxygen can be obtained from air. Most of the fuel cells are supplied with hydrogen and air streams. As mentioned previously, hydrogen production, storage, and transportation represents a significant problem for fuel cell technology. Therefore, the production of hydrogen gas for the fuel cells has been an important field of research and development. Presently, approximately 95% of hydrogen produced in the world comes from reforming of fossil fuels (gasoline, natural gas, and oil) and the rest are from other methods [73, 74].

Reforming fossil fuels for hydrogen production has been achieved by steam reforming, partial oxidation, and coal gasification [75–80]. Hydrocarbons are used in the reforming processes to produce hydrogen, especially methane (CH_4) and methanol (CH_3OH). In the steam reforming method any hydrocarbon (C_nH_m) is capable of being reformed to produce hydrogen and carbon dioxide. The carbon dioxide produced is further converted into hydrogen using a water gas shift reaction. In the partial oxidation method, methane is the main raw material to be reformed into hydrogen gas. As the name suggests, the coal gasification process combusts coal, carbon material, and biomass in order to produce gaseous products. This gas product is composed of carbon dioxide, carbon monoxide, hydrogen, nitrogen, methane, and hydrogen sulfide. In all of the reforming methodologies, purification of hydrogen gas is necessary to meet the requirements of the fuel cells. Purification process is an additional, and energy consuming, step for hydrogen production. So, certain fuel cells, such as DMFC, MCFC, and SOFC, can use methanol as the fuel as

well as tolerate some percentage of carbon monoxide and carbon dioxide along with a hydrogen stream.

One of the alternate methods used for the production of hydrogen is electrolysis, which has been primarily focused on water electrolysis. The electrolysis of water or other alternate hydrogen sources, such as ammonia, urea, and coal, are discussed in detail in the later section, “Trends: Novel Electrosynthesis Processes.” As described in Fig. 38.1, the synthesis of chemicals using electrochemical methods, where the chemicals synthesized has the capability to produce energy or power. These chemicals store energy in their chemical bonds, so the electrochemical synthesis of the hydrogen gas can also contribute towards electrochemical energy storage systems.

Supercapacitors

After batteries, supercapacitors are considered the next most important device in the area of electrochemical storage. Supercapacitors are also known as ultracapacitors, EDLC, or electric double-layer capacitors. The EDLC has electrodes similar to the conventional electrostatic capacitor, but the capacitance for the EDLC is measured due to the presence of a liquid electrolyte (Fig. 38.8). The electrostatic capacitor is the conventional form of the capacitor where the electrodes are separated by non-polarized materials, such as vacuum or air or mica. A supercapacitor is composed of two electrodes and an electrolyte, such as a battery, but the electrode/electrolyte interface is a capacitor, which is the equivalent of a complete cell with two capacitors in series [29].

Ultracapacitors fall in-between electrostatic capacitors and batteries as they have higher power density (10 kW/kg) than batteries, and also more specific energy density than conventional capacitors. On the contrary, supercapacitors have less energy density (about 5 Wh/kg) when compared to 30–40 Wh/kg from a typical LAB [81]. Figure 38.9 displays a plot of specific power density vs. specific energy density for some energy storage devices.

Ultracapacitors have a longer cycle life than any kind of battery and they can also be more quickly charged than most of the batteries. Supercapacitors are generally divided into three different types based on the charge storage process. The types are double layer capacitors, redox-based electrochemical capacitors, and hybrid capacitors. Carbon derived from charcoal, such as activated carbon, is used as the active material in the electrode for supercapacitors. The electrolyte used for double layer capacitors is either sulfuric acid or organic liquid. The capacitance for double layer capacitors in organic electrolytes has reached 100–120 F/g, but it can be 150–300 F/g in aqueous electrolytes, with the exception that a lower cell voltage has to be maintained to avoid water decomposition [81].

Redox-based electrochemical capacitors are the devices in which fast and reversible redox reactions takes place on the surface of the active material. The active materials used in these capacitors are metal oxides, such as RuO₂, Fe₃O₄, MnO₂, and conducting polymers. Most commonly, RuO₂ has been investigated because it has three distinct oxidation states within 1.2 V. The redox reaction for the RuO₂ active material is fast and reversible, where RuO₂ reacts with protons by electro-adsorption of protons on its surface (38.74). RuO₂-based electrochemical capacitors have displayed a capacitance of more than 600 F/g.



A hybrid capacitor is the most recent electrochemical capacitor which combines a capacitor-like electrode with a battery-like electrode in order to obtain both high power and energy density systems. This concept of hybrid capacitors is based on Li-ion capacitors. In 1999, Amatucci’s group developed a hybrid capacitor with nanostructured lithium titanate (Li₄Ti₅O₁₂) anode and activated carbon cathode, which was able to deliver a specific energy density of at least 10 Wh/kg at 2.8 V [82]. Recently, this material, Li₄Ti₅O₁₂, has been investigated by combining the material with carbon nanofibers in order to produce nanohybrid capacitors [28].

Applications of supercapacitors have been mainly in the consumer electronics area, but more research is currently focused on combining supercapacitors with battery packs in order to provide stable and on-demand power supplies for electric vehicles.

Industrial Electrosynthesis Processes

As discussed previously, under the vision described in Fig. 38.1, electrochemical synthesis can be viewed as a way to store energy, as renewable and/or intermittent electrical power could be used to store energy as chemicals, products, commodities, fuels, etc. Industrial electrosynthesis had been used in different large-scale processes, including: chlorine and sodium hydroxide production, aluminum production, metal winning and refining, hydrogen and oxygen production, and specialized synthesis of organics. This section describes some of these processes. Further reading can be found in the literature [8, 12, 21, 83–95].

Chlor-Alkali Process

One of the largest electrochemical operations in the world is the chlor-alkali process or technology. The industry based on the chlor-alkali technology has been around for more than

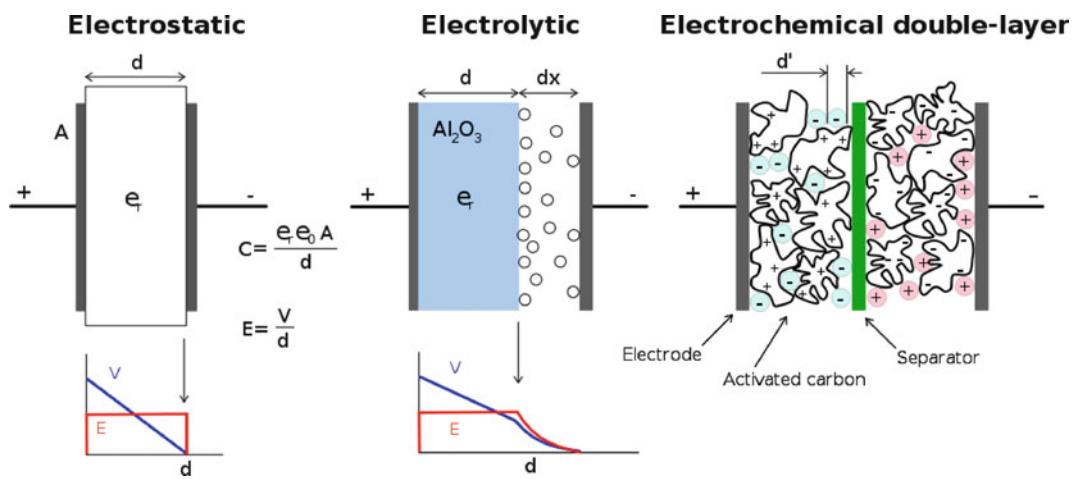


Fig. 38.8 Comparison of three kinds of capacitors [141]. The three types of capacitors are electrostatic, electrolytic, and electrochemical double-layer. The material in-between the positive and negative terminal determines the type of capacitor

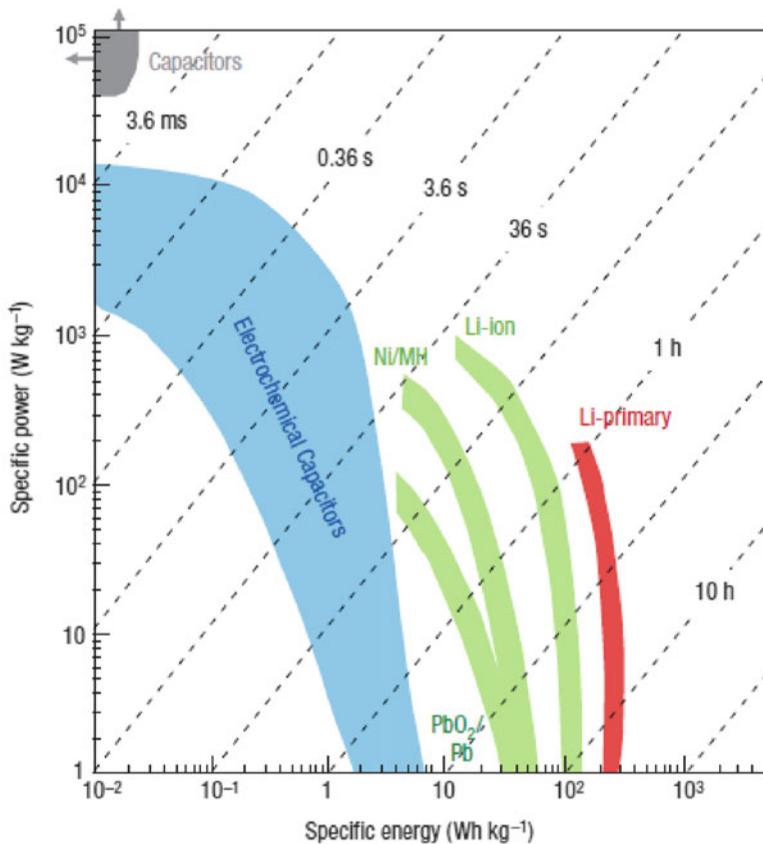


Fig. 38.9 Specific power vs. specific energy (Ragone plot) for energy storage devices [81]. Batteries have high specific energy density but low specific power density. Conversely, the traditional capacitors have very high power density and very low energy density. Electrochemical

capacitors have the potential to possess optimum level power and energy density. *Legends*— PbO_2/Pb lead acid batteries; Ni/MH nickel metal hydride batteries; Li-ion lithium ion batteries; Li-primary lithium-based primary batteries

100 years. The chlor-alkali process produces chlorine and sodium hydroxide (caustic soda) from the electrolysis of sodium chloride or brine solution. A detailed description of the chlor-alkali technology with its accompanying history,

advancements in different electrochemical cells used in the process (including their design), and engineering principles needed to establish chlor-alkali processing plants is available for further reading in the literature [12, 83, 84].

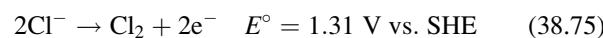
Among the electrochemical methods for producing chemicals, chlor-alkali technology consumes the second largest amount of electricity or electrical energy [86]. Chlorine and caustic soda are critically important chemicals in the world, and they are used in the production of various other chemicals and products which are used in everyday life. Production of more than 95% of chlorine and 99.5% of caustic soda are from the electrochemical method. Chlorine production capacity in the world was 22 million tons in 1970 and it increased to 53 million tons in 2002 [84]. The production of chlorine and caustic soda using this process is another example of the vision described in Fig. 38.1, storing electrical energy in the form of valuable chemicals. The chlorine is used in the manufacture of the polymer polyvinylchloride (PVC), and in the preparation of organic solvents (e.g., methylene chloride, chloroform, carbon tetrachloride), organic compounds (e.g., chlorobenzenes, alkyl chlorides), and inorganic compounds (e.g., hypochlorites of sodium, calcium). The bleaching property of the chlorine is used in the paper and pulp industry, and employed as an oxidizing agent in water treatment operations [12, 84]. The use of sodium hydroxide or caustic soda has been in the paper and pulp industry, soap and detergents manufacturing, and textile industry, as well as in the aluminum extraction process [12, 84].

The electrolysis of sodium chloride solution results in the formation of chlorine and hydrogen gases, and of sodium hydroxide. In 1800, Cruikshank discovered the electrolysis of brine in order to produce chlorine, but it took a relatively long time to scale up this process to manufacturing scale [84]. Development of the chlor-alkali process is attributed to the improvement of the electrolysis cell and its operation. There are three different types of cells used in the chlor-alkali technology, namely the diaphragm cell, the mercury cell, and the membrane cell. In 1855, the diaphragm cell process (Griesheim Cell) was introduced. At the same time, development of the mercury cell process led to the industrialization of the Castner-Kellner cell, which took place in 1892. Finally, in the early 1970s, the membrane cell process was developed as the modification to the diaphragm cell [85]. The current efficiency for the chlor-alkali process has been in the range of 85–98% depending on the type of the cell, operation of the electrolyzer, and purity of the brine solution. The electrical energy demand for performing electrolysis under different types of chlor-alkali technologies are 3,100–3,400 kWh/ton of Cl_2 for the mercury cell process, 2,300–2,900 kWh/ton of Cl_2 for the diaphragm cell process, and 2,100–2,900 kWh/ton of Cl_2 for the membrane cell process [85]. The schematic diagram of the three different cell processes of the chlor-alkali technology is displayed in Fig. 38.10. Brief descriptions of these three different cell designs are presented next.

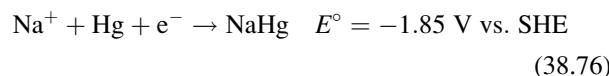
Mercury Cell

The mercury cell is an undivided cell, as shown in Fig. 38.10, where the base of the container is made of steel in order to provide the electrical contact for the cathode. The cathode for the mercury cell process is liquid mercury (Hg), which is kept flowing during electrolysis. The anode electrode for the mercury cell process is a coated expanded titanium dimensionally stable anode (DSA). The anodes are left in a suspending manner on the top of the container or electrolyzer such that they are parallel to the pool of the Hg cathode. The electrolyte for the mercury cell is a brine (NaCl) solution. The saturated brine solution (25% NaCl), at a temperature of 60°C, is supplied to the top of the electrolyzer. With the electrolysis, the concentration of the brine solution is reduced in the mercury cell. The depleted brine solution (17% NaCl) is removed from the container just above the top of the mercury electrode. The electrochemical reactions taking place at the electrodes in the mercury cell are given below: [12]

Anode reaction



Cathode reaction

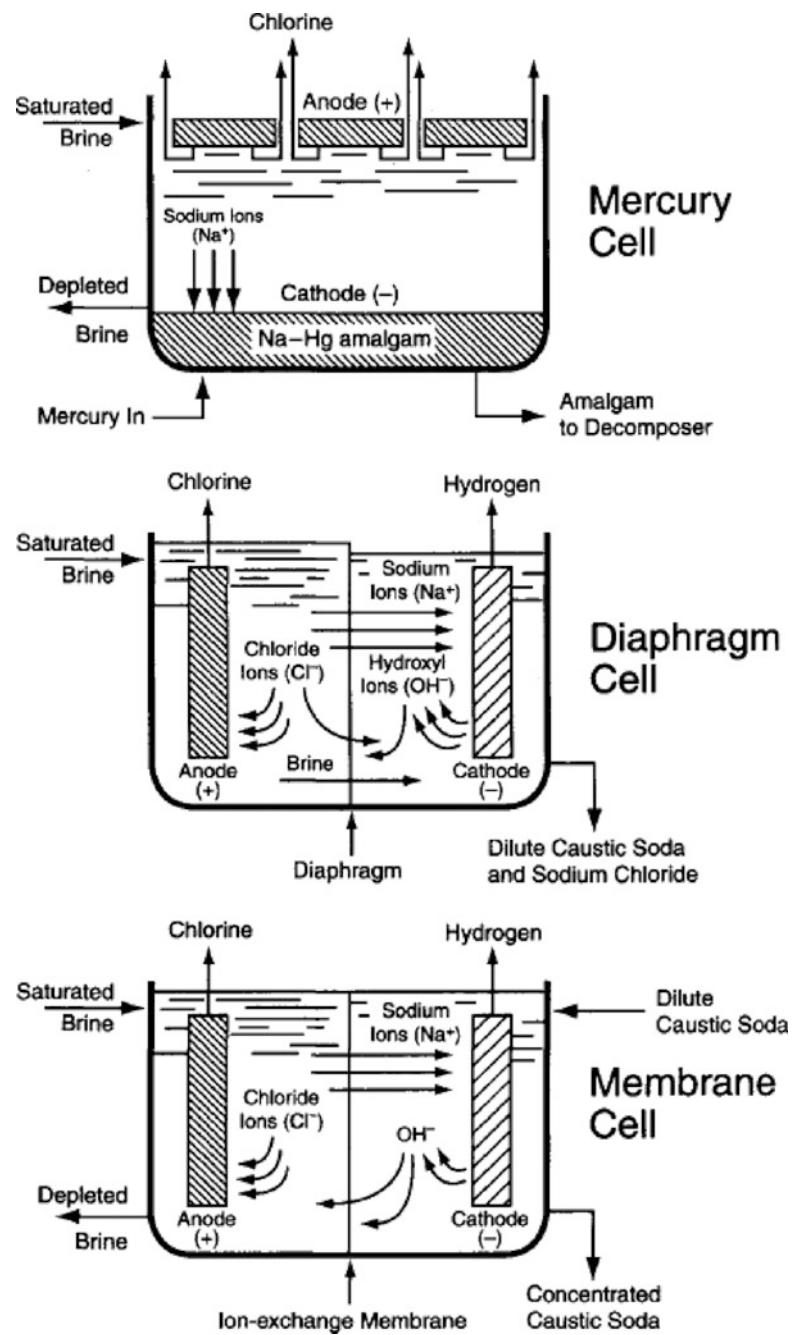


At the anode, the chloride ions are oxidized to a chlorine gas, which at first saturates the electrolyte solution before escaping the mercury cell. The Na^+ ions present in the electrolyte migrates to the Hg cathode where they are reduced to form an amalgam. The overall voltage for the reactions at the electrodes is 3.16 V but typical operation of the mercury cell requires 4.50 V due to the resistance from electrical contacts. This amalgam containing liquid Hg, from the mercury cell, is taken into a container known as a decomposer or denuder. In the decomposer, the mercury is recovered from the $\text{Na}(\text{Hg})$ amalgam and sent back to the electrolyzer in order to use it as cathode. The $\text{Na}(\text{Hg})$ amalgam, in the decomposer, trickled along with water over the graphite particles containing transition metals (e.g., Fe and Ni) to obtain sodium hydroxide and mercury (38.77) [86].



One of the issues with the mercury cell electrolyzer is the health and environmental damages associated with mercury. The mercury cell was widely used in many countries for the production of chlorine and caustic soda during the early days of the chlor-alkali industry. In 1984, 45% of the chlor-alkali plants in the world employed mercury cell processes and its

Fig. 38.10 Schematic diagram of the three different cells used in the chlor-alkali technology [84]. The mercury, diaphragm, and membrane cells are depicted with the flow of brine solution, flow of ions across the cells, and production of chlorine, hydrogen, and sodium hydroxide



percentage declined to only 18% in 2001 due to the health and environmental concerns of using mercury [84]. In fact, presently there are no functioning mercury cell type chlor-alkali plants in Japan and many countries are planning to gradually phase out the mercury cell process.

Diaphragm Cell

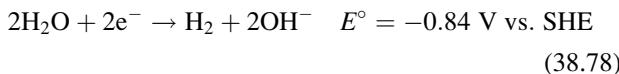
This process uses a divided cell, where a diaphragm is used to separate the anode side from the cathode side. Asbestos as diaphragm was used in the earlier days before the knowledge of the detrimental health effects of asbestos was known.

Now, non-asbestos-based diaphragm are used in the construction of the diaphragm cells and plans are being taken to convert all the diaphragms to non-asbestos material.

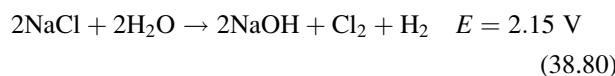
Saturated brine solution is fed to the anode compartment of the diaphragm cell, where the chloride ions are oxidized to a chlorine gas as shown in the (38.75). The brine solution flows from the anode to cathode side through the diaphragm. The anodes used in the diaphragm cell process have either ruthenium-based or platinum/iridium-based coated titanium electrode (DSA) [86]. During the electrolysis, the temperature of the electrolyte is maintained between ~95 and 100°C.

On the cathode side, hydrogen gas is generated from the reduction of water (38.78) even using a nickel electrode. The Na^+ ion from the anode compartment migrates through the diaphragm into the cathode side to combine with hydroxyl ion from water reduction reaction to form sodium hydroxide (38.79).

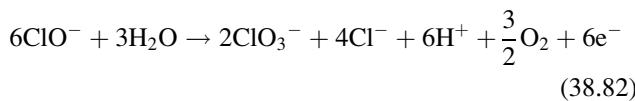
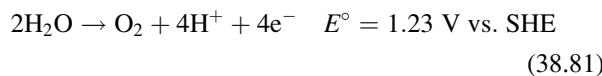
Cathode reaction



Overall reaction



The voltage for the electrolysis of brine to produce caustic soda, chlorine, and hydrogen is 2.15 V. However, the normal operational cell voltage for this process is in the range of 3.2–3.8 V, so as to overcome the resistance encountered during the electrolysis [12]. In this process, the cathode electrolyte solution with concentration of 12% NaOH and 15% NaCl is taken for further processing to separate the caustic soda from brine solution for commercial application [86]. The purpose of the diaphragm in this cell is to allow the passage of Na^+ ions from the anode to cathode side but also to avoid the mixing of caustic soda with chlorine. Still there are two parasitic reactions possible on the anode electrode, namely the formation of oxygen along with chlorine (38.81) and oxidation of hypochlorite to chlorate (38.82) [86].



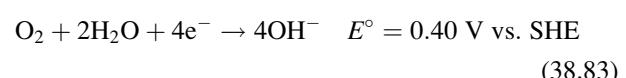
Membrane Cell

The operation of the membrane cell electrolyzer is similar to the diaphragm cell process except for the ion exchange membrane being used in place of a diaphragm. The ion exchange membrane used in the electrolyzer is commercially known as Nafion, which is sulfonated tetrafluoroethylene-based fluoropolymer-copolymer. The electrochemical reactions at the anode and cathode electrodes for the membrane cell process are same as in the diaphragm cell process. The brine solution used as electrolyte for this process should have less than 0.1 ppm Ca^{2+} and Mg^{2+} ions to avoid

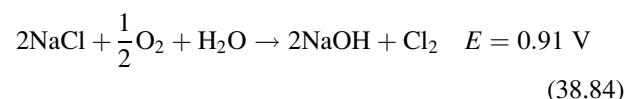
precipitation of salt over the electrodes and the ion exchange membrane [86]. The saturated brine solution is added to the anode compartment and only the Na^+ ions along with water molecules are migrated across the Nafion membrane to the cathode side. The depleted brine solution is removed from the anode compartment. On the cathode side of the membrane cell, solution containing dilute concentration of caustic soda is added to increase the concentration of caustic soda in the product stream.

High purity of caustic soda, up to 50% NaOH, can be produced in the cathode compartment using this membrane cell process as the chloride ions are not migrated to the cathode side. However, in practice, 32–35% NaOH is normally produced on the cathode compartment from this process. Another interesting feature of this process is the distance between the anode and cathode electrode can be reduced to almost zero because of the use of ion exchange membrane. This option of sandwiching the electrodes with Nafion membrane has resulted in operating cell voltage of ~2.7 V compared to 3.2–3.8 V for diaphragm cell process. This means the membrane cell process will consume less energy than diaphragm cell process [12].

A new approach is being investigated in the membrane cell process for reducing the energy consumption of the electrolysis and also to avoid the production of hydrogen gas at the cathode. In the chlor-alkali industry, importance is given towards the production of caustic soda and chlorine from the electrolysis of brine (NaCl), but not as much importance as is given for hydrogen generation. So, the evolution of hydrogen gas at the cathode electrode is considered an undesired reaction. The approach is to use oxygen-depolarized cathode (ODC) electrode to avoid hydrogen formation at cathode by reduction of oxygen in the presence of water to form hydroxyl ions (38.83). The ODC is made of GDE which is normally used in the fuel cells [85].



Now combining the above cathode reaction with the oxidation of chloride ion to chlorine at the anode (38.75) and formation of NaOH with Na^+ ions (38.79), we obtain the overall reaction for the electrolysis of brine using ODC electrode as



From the (38.84), the voltage for the overall reaction is only 0.91 V compared to 2.15 V for the traditional membrane cell process. The use of ODC electrode has resulted in

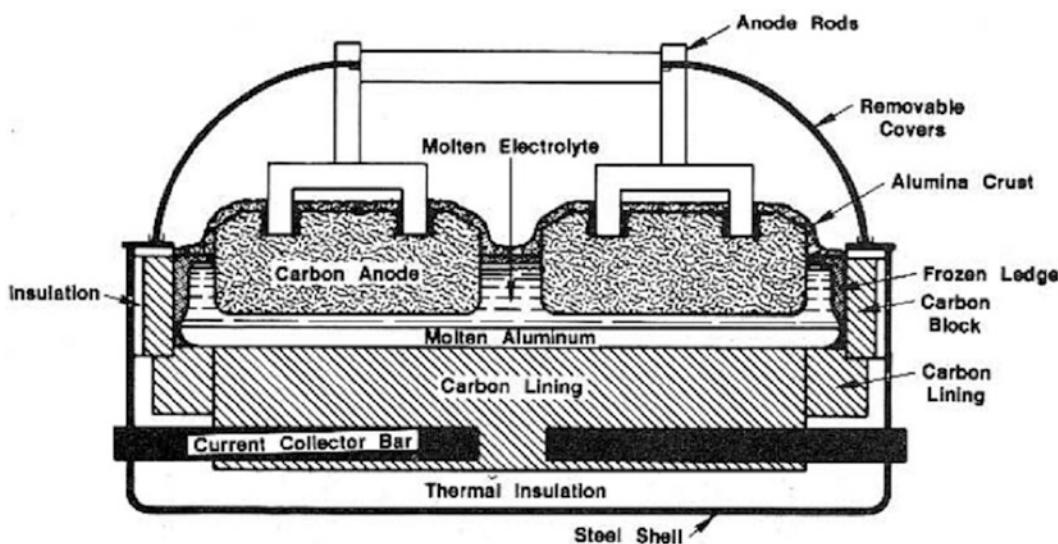


Fig. 38.11 Cross-sectional view of the electrolytic cell to produce aluminum [87]. Prebaked anodes are used in this type of electrolytic cell. Molten aluminum is produced from the Hall-Heroult process

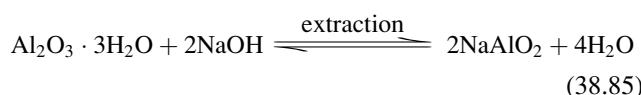
the operation cell voltage of a mere 1.23 V for the new membrane cell process, which translates to almost 30% less electric energy consumption than the traditional approach of membrane cell where hydrogen gas is produced [85]. A detailed description on the development of the ODC electrodes with different catalyst and design of the electrolyzer can be found in the literature [85].

Aluminum Production

Aluminum is the third most abundant element in the Earth's crust. Since aluminum can easily react with oxygen, it does not exist in metallic form in the Earth's crust but in the form of ores, such as bauxite. The valuable properties of aluminum are its being soft, durable, lightweight, electrically conducting, nonmagnetic, stiffness equivalent to steel, and corrosion resistant. These favorable characteristics have resulted in various uses for aluminum. Aluminum has found application in the areas of transportation, packaging (e.g., beverage cans), construction, electronics, and electrical wires.

Electrochemical method of producing aluminum was not effective until 1886, when Charles Martin Hall from Ohio, USA, and Paul L. T. Heroult from Paris, France, independently invented the electrolytic way of extracting aluminum from its molten salt. The Hall-Heroult process, which is widely used throughout the world, for aluminum production has been a very reliable and efficient method for the past 125 years. Over these years, the process has undergone technological improvements mostly in the anode material [22]. This process involves electrolysis of alumina (Al_2O_3),

which is dissolved in molten cryolite-based electrolyte. Alumina for the Hall-Heroult process was obtained from the aluminum ore, bauxite, using the Bayer process. In the Bayer process, the bauxite ore, which has almost 50% Al_2O_3 , was digested in sodium hydroxide (NaOH) solution under pressure resulting in the formation of sodium aluminate and the impurities were left behind as red mud (38.85).



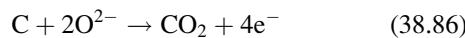
The aluminate solution was seeded with hydrated alumina crystals to re-precipitate alumina, which can easily be washed. In the final step, the hydrated alumina was calcined at 1,200°C to remove water vapor and obtain more than 99% pure alumina [12, 83].

In the Hall-Heroult process, the electrolytic cell is called as pot and a cross-sectional view of the electrolytic cell is shown in Fig. 38.11.

In this process, the anode electrode, mainly made of carbon, is consumed during the electrolysis of alumina. The electrolytic cells are differentiated by the kind of anode electrodes used. There are two kinds of anodes in the Hall-Heroult process, prebaked and self-baking, or Söderberg anodes. Both kinds of anodes are made of petroleum coke and coal tar, where the prebaked anodes are baked in brick lined pits before using in the electrolytic cells. However, the Söderberg anodes are allowed to bake in the cell using the heat from the electrolysis of alumina. In Fig. 38.11, the electrolytic cell has a steel shell container which is lined with carbon to act as the cathode for the electrolysis.

The electrolyte has alumina, from the Bayer process, mixed with molten cryolite (Na_3AlF_6) solution. Calcium fluoride is also included as an additive. The ratio of the sodium fluoride to aluminum fluoride is maintained at 1.5 in the molten electrolyte. The temperature of the electrolytic cell was maintained in the range of 920–980°C in order to keep the electrolyte in molten condition. Even though the Hall-Heroult process is 125 years old, the explanation for the electrode reaction mechanism has not been clearly documented due to the complex nature of the electrolyte and the possibility of having various species in the electrolyte. The readers are advised to check this literature to understand the complex nature of the ions present in the electrolyte and their reactions [87]. A simplistic explanation would be that the alumina dissociates into aluminum ion and oxide ion in the molten electrolyte. At the cathode, the aluminum ion is reduced to liquid aluminum metal at the operating temperature and collected on top of the cathode electrode. At the anode electrode, oxide ion is oxidized to oxygen gas, which reacts with the carbon anode to form carbon dioxide. So, the overall reaction would be alumina reacts with carbon to form metallic aluminum and carbon dioxide [12].

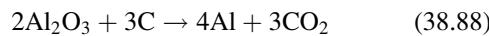
Anode reaction



Cathode reaction



Overall reaction

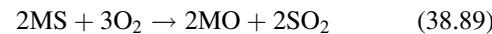


The cell voltage for the overall reaction is 1.18 V, but due to the electrolyte resistance and other voltage drops, the operating voltage required for aluminum production ranges from 4.0 to 4.5 V [12]. In 1914, on average 59 kg of Al was produced per day from a plant operating at 10 kA and 8 V with 73.3% as current efficiency. Over the years, the production capacity of the Hall-Heroult process has improved to 2,308 kg of Al per day, in 2000, at 300 kA and 4.2 V operating condition with a current efficiency of 95.6%. Still, among the electrolytic processes, the production of aluminum is the highest energy consuming process, which translates into high demand for electricity by this technology. During this period, the energy requirement has become better, from 32.53 kWh in 1914 to 13.10 kWh for every kilogram of Al produced in 2000 [22].

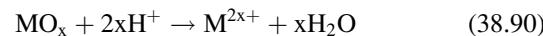
Electrowinning and Refining Process

The process of extracting metals from its ores using the electrochemical method is known as electrowinning.

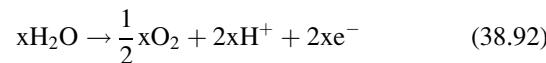
The electrowinning method is the last step in the entire extraction process of a metal from its ore. The ores of a metal are generally in the form of metal sulfides or oxides or mixture of both. For simplicity, let us consider the sulfide form of the metal as the ore to be used in the extraction process. The sulfide ore will be converted into oxide form by roasting the metal ore in the air [12].



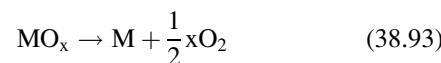
The oxide salt of the metal is leached or dissolved in acid solution especially with sulfuric acid to form acid solution containing metal ions [83].



In fact, the acid solution contains different metal ions from the ore along with the desired metal ion, so the solution is purified and subsequently concentrated with the desired metal ions. The electrowinning process is basically the electrolysis of the acid solution, where the metal ions are reduced into metal on the cathode electrode (38.91) and the oxygen gas is evolved at the anode (38.92).



Along with the oxygen gas, the protons or acid is formed at the anode electrode, which will be recirculated for leaching the metal oxide ores. The overall reaction of the electrowinning process is the deposition of the metal and the release of oxygen gas (38.93). There is no loss of water or the acid in this electrowinning process.



The few elements that can be electrowon under aqueous conditions are copper (Cu), silver (Ag), nickel (Ni), cobalt (Co), chromium (Cr), and zinc (Zn). However, the highly reactive elements, such as lithium (Li), sodium (Na), magnesium (Mg), and aluminum (Al), needs molten electrolyte to extract them using the electrowinning process. Electrolysis of alumina to produce aluminum is also considered as the electrowinning process for aluminum metal, and a detailed description of this process was provided in the above section, “Aluminum Production.” The electrochemistry of extracting the above listed elements can be found in the literature [12, 83]. In addition to extracting the metal from its ores, the electrowinning process is used to recover the metals from industrial wastewater in order to eliminate or reduce the metal contamination in the wastewater.

The electrolytic process to refine or increase the purity of the metal is defined as electrorefining, and this method is employed in the metallurgy industry. The impure metal is taken as anode of the electrolytic cell and the electrolyte is the solution of that metal salt. During the electrolysis process, the desired metal is oxidized into metal ion at the anode (38.94), which dissolves into the electrolyte. At the same time, the pure metal is deposited over the cathode by reducing the metal ion from the electrolyte (38.95). The anode and cathode reactions ((38.94) and (38.95), respectively) are reversible reactions, which should result in a net zero cell voltage.



But in practical applications, the electrolytic cells used for the electrorefining processes require certain cell voltage. The cell voltage was necessary to overcome the solution resistance, voltage drops at the electrical contacts for the anode and cathode, and the overpotentials for both reactions (anodic and cathodic) to take place at a reasonable rate. At the anode electrode, metals nobler than M will be oxidized and retained in the electrode as residue, which is commonly known as the anode slime. But those metals which are less noble than M, after undergoing oxidation will be dissolved into the electrolyte as contaminants. These contaminants present in the electrolyte are not reduced onto the cathode before the reduction of metal M, and the undesired metal can build up during the electrorefining process thereby increasing the impurity.

In the electrorefining process, the use of aqueous electrolyte has been applied for elements, such as copper, nickel, cobalt, lead, silver, gold, and tin. The refining process for the copper metal is extensively used in the production of high purity copper metal for electronics applications. Similarly in the jewelry industry, the electrorefining process is used to remove or extract the noble metal (e.g., gold) from the anode slime or contaminated solutions. Electrorefining of aluminum is performed using the molten electrolyte, which is mainly applied for the recycling of waste aluminum scrap metal. More detailed information on the electrorefining process can be obtained in the literature [12, 83].

Hydrogen and Oxygen Production

Manufacturing of gases like hydrogen and oxygen is also accomplished using electrochemical methods. Hydrogen gas is formed as a by-product during the electrolysis of a brine solution in the chlor-alkali process. Depending on the type of the chlor-alkali cell, the hydrogen gas is purified for

commercial applications. However, the water electrolysis process is entirely committed for the production of both hydrogen and oxygen gases with highest purity. A detailed description on the science and the electrochemical reactions associated with the electrolysis of water is explained in the following section, “Electro-Synthesis of Hydrogen.”

In 1800, Nicholson and Carlisle discovered the splitting of water into hydrogen and oxygen [21, 83]. The development and commercialization of water electrolyzers for the industrial scale began in the 1920s and 1930s [90]. During that time several 100 MW electrolyzers were built around the world for ammonia fertilizers and petroleum refining [21, 90]. Among the notable installations of the water electrolyzers was at the Aswan High Dam site in the late 1980s with 144 electrolyzers, which was rated at 162 MW and a capacity to produce 32,400 m³/h of hydrogen gas [21]. The cell designs used for the electrolyzer were monopolar electrodes in tank electrolyzers and bipolar electrodes in a filter press cells. High pressure electrolyzers were also tested and commercially produced. One of the industrial water electrolyzers manufactured by DeNora Impianti Electtrochimici S.p.A. is shown in Fig. 38.12.

The details of other commercially available water electrolyzers with their operation parameters are listed in Table 38.9 [21].

Organic Electrosynthesis

The synthesis of organic compounds was traditionally favored through chemical routes. From the beginning of the last century, however, the use of electrochemical reactions to synthesize organic compounds has been practiced for various reasons. The advantages on using the electrochemical synthesis method include: (1) product selectivity and purity is higher than for chemical synthesis, (2) less reaction steps are needed than for the chemical method, (3) inexpensive starting materials are used, (4) least polluting chemicals or by-products are formed, (5) less hazardous routes are involved, and (6) less energy is consumed [93, 96].

The electrosynthesis processes for organic compounds also have disadvantages or limitations in terms of selecting the electrode material and the electrolyte composition, because generally aqueous electrolytes are used in electrochemical synthesis, but solubility of organic compounds in aqueous solutions has to be sorted out. Some of the shortcomings of the electrochemical processes to synthesize organic compounds have been the discovery of an alternate catalytic route (sorbitol and propylene oxide), an alternate chemical route was discovered to avoid the electrochemical intermediate product (pinacol), the formation of a pollutant product (tetraalkyl lead), and the product had lost its market or the market never existed [93].

Fig. 38.12 Bipolar electrolyzer manufactured by DeNora Impianti Electtrochimici S.p.A. This unit has 54 cells, operated with a current of 2.5 kA, power consumption was approximately 4.6 kWh N/m³ and the total capacity of the electrolyzer was 250 kW [90]

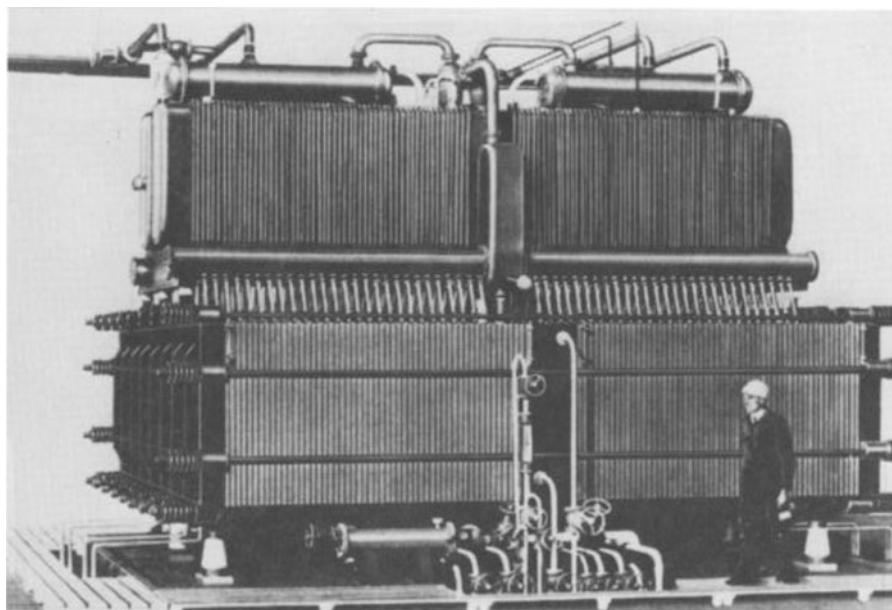


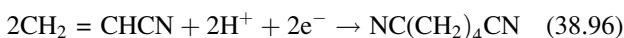
Table 38.9 Water electrolyzers and other their operating conditions

Parameter	De Nora S.p.A.	Norsk hydro	Electrolyzer Corp. Ltd.	Teledyne energy systems	General electric
Cell type	B-FP	B-FP	M-T	B-FP	B-FP
Anode	Expanded Ni-plated mild steel	Activated Ni-coated steel	Ni-coated steel	Ni screen	PTFE-bonded noble metal
Cathode	Activated Ni-plated steel	Activated Ni-coated steel	Steel	Ni screen	PTFE-bonded noble metal
Pressure (MPa)	Ambient	Ambient	Ambient	0.2	0.4
Temperature (°C)	80	80	70	82	80
Electrolyte	29 % KOH	25 % KOH	28 % KOH	35 %	Nafion
Current density (A/m ²)	1,500	1,750	1,340	2,000	5,000
Cell voltage (V)	1.85	1.75	1.9	1.9	1.7
Current efficiency (%)	98.5	98.5	>99.9	NR	NR
Oxygen purity (%)	99.6	99.3–99.7	99.7	>98.0	>98.0
Hydrogen purity (%)	99.9	98.9–99.9	99.9	99.99	>99.0

B-FP bipolar electrodes in filter press cells; M-T monopolar electrodes in tank cells

Source: Zeng and Zhang [21]

One of the well-known organic compounds electrochemically synthesized is adiponitrile. The chemical adiponitrile is an intermediate in the production of Nylon 66. In 1959, Manuel Baizer at Monsanto discovered the process to produce adiponitrile by the electrochemical method of hydrodimerization of acrylonitrile at the cathode. This method was later known as the Monsanto process. "More details and progress on the Monsanto process can be gathered from the literature [12]. In the Monsanto process, oxygen gas is evolved at the anode, while at the cathode acrylonitrile is electrohydrodimerized to adiponitrile, as shown below: [93]



The Monsanto plant at Decatur, Alabama, USA, is capable of producing 200 million kg of adiponitrile per year. The cathode used for this process is cadmium and the anode is a steel electrode, which are both assembled in a bipolar way in an undivided cell. The electrolyte comprises acrylonitrile, a quaternary salt (hexamethylene(bisethylbutyl)ammonium phosphate), phosphate buffer, and the anode anticorrosive additives, borax, and EDTA. A current density of 2 kA/m² is maintained at 55°C operating temperature and the process has a power consumption of 2.4 kWh/kg of adiponitrile produced [93, 96]. Table 38.10 provides a list of various organic compounds manufactured in the world using the electrosynthesis approach; some of these processes are commercialized, others in the pilot stage, and some of them are decommissioned.

Table 38.10 List of some organic compounds produced using industrial electrosynthesis

Product	Starting material	Company	Operating status
Acetoin	Butanone	BASF	C
1-Acetoxy naphthalene	Naphthalene	BASF	P
Acetylenedicarboxylic acid	1,4-Butynediol	BASF	C
Adipoin dimethyl acetal	Cyclohexanone	BASF	C
Adiponitrile	Acrylonitrile	Monsanto (Solutia), BASF, Asahi Chemical	C
2-Aminobenzyl alcohol	Anthranilic acid	BASF	P
4-Aminomethylpyridine	4-Cyanopyridine	Reilly Tar	C
Anthraquinone	Anthracene	L. B. Holliday, ECRC	C
Anthraquinone	Naphthalene, butadiene	Hydro Quebec	P
Arabinose	Gluconate	Electrosynthesis Co.	P
Azobenzene	Nitrobenzene	Johnson Matthey Company	C
Calcium gluconate	Glucose	Sandoz, India	C
Calcium lactobionate	Lactose	Sandoz, India	C
S-Carbomethoxymethylcysteine	Cysteine + chloroacetic acid	Spain	C
Diacetone-2-ketogulonic acid	Diacetone- <i>L</i> -sorbose	Hoffman-LaRoche	C
Dialdehyde starch	Starch	CECRI	C
3,6-Dichloropicolinic acid	3,4,5,6-Tetrachloro-picolinic acid	Dow	P
1,4-Dihydronaphthalene	Naphthalene	Clariant	C
1,2-Dihydrophthalic acid	<i>o</i> -Phthalic acid	BASF	D
2,5-Dimethoxy-2,5-dihydrofuran	Furan	BASF	C
Ethylene glycol	Formaldehyde	Electrosynthesis Co.	P
Gluconic acid	Glucose	Sandoz, India	C
Glyoxylic acid	Oxalic acid	Rhone Poulenc, Steetley	P
Hexafluoropropyleneoxide	Hexafluoropropylene	Clariant	C
Monochloroacetic acid	tri- and di-Chloroacetic acid	Clariant	P
Mucic acid	Galacturonic acid	EDF	C
Nitrobenzene	<i>p</i> -Aminophenol	India, Monsanto	P
5-Nitronaphthoquinone	1-Nitronaphthalene	Hydro Quebec	P
Partially fluorinated hydrocarbons	Alkanes and alkenes	Phillips Petroleum	P
Perfluorinated hydrocarbons	Alkyl substrates	3M, Bayer, Clariant	C
Pinacol	Acetone	BASF, Diamond Shamrock	P
Piperidine	Pyridine	Robinson Bros.	D
Polysilanes	Chlorosilanes	Osaka Gas	C
Salicylaldehyde	<i>o</i> -Hydroxybenzoic acid	India	C
Sorbitol	Glucose	Hercules	D
Substituted benzaldehydes	Substituted toluenes	Hydro Quebec, W.R. Grace	P
Succinic acid	Maleic acid	CERCI, India	C
Tetraalkyl lead	Alkyl halide	Nalco	D

C commercial process; P pilot process; D discontinued commercial process

Source: Sequeira and Santos [93]

Trends: Novel Electrosynthesis Processes

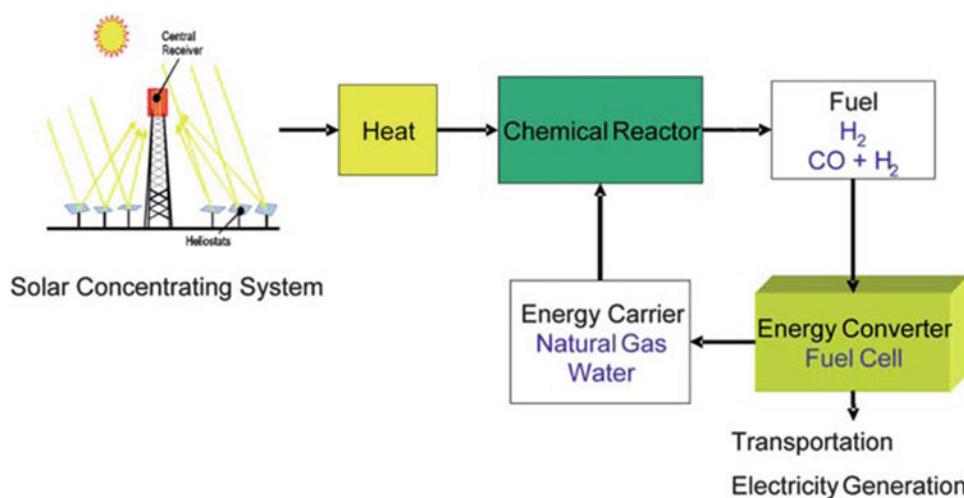
The latest processes involved in the electrosynthesis of chemicals which have potential for power generation, and water and air remediation are discussed in this section. The new interest in utilizing solar energy to manufacture chemicals capable of being used as fuels has caught the attention of many researchers. Additionally, the electrochemical approach to synthesize hydrogen from various chemicals (water, ammonia, urea, and coal) is also described in this section. The main focus of the electrolysis of ammonia and urea has been to remediate the ammonia and urea

rich wastewater. The hydrogen gas produced during the ammonia and urea electrolysis process is considered as high value by product. The advantage of coal electrolysis is to reuse the coal waste for the production of hydrogen, and also to generate other chemicals which have potential to be classified as liquid fuels.

Solar Fuels

In recent years, a new area of research has been devoted towards producing liquid fuels, which can be used for

Fig. 38.13 Schematic diagram for the concept of solar fuel production [142]. The heat from the concentrated solar power plant is used in the chemical reactor to produce fuels, such as H_2 and syn gas ($CO + H_2$). The fuels produced from the chemical reactor will be utilized in fuel cells for power generation or transportation applications. Alternatively, the hydrogen can be combined with CO and CO_2 to form hydrocarbons, such as methane



generating energy or power from solar energy. These fuels are referred to as “solar fuels,” because the energy needed to produce them comes from the sun. Solar fuels can be used as raw materials for manufacturing different kinds of chemical products as well as generating power. In this way, solar fuels can be considered energy carriers.

The methodology adapted to produce solar fuels was to utilize solar energy through solar cells in order to split water into oxygen and hydrogen. The hydrogen gas produced from water electrolysis is combined with carbon dioxide and/or carbon monoxide found in industrial effluents to produce hydrocarbons, which are referred to as “solar fuels.” This method not only uses renewable energy sources to produce chemicals that have properties as fuel, but it also converts pollutants present in industrial effluents into useful products.

The solar energy is collected in large power plants, known as concentrating solar power plants (CSP). These systems are being built around the world in regions of relatively high solar radiation. A schematic diagram illustrating the idea of using solar energy obtained from the concentrated solar power plant for the production of solar fuels is shown in Fig. 38.13. The concept involves solar thermochemical cycles to produce hydrogen from solar steam forming of natural gas and methane cracking.

The splitting of water using solar energy is also achieved by photoelectrochemical (PEC) and photocatalytic methods [97]. In the photocatalytic method, the catalyst material is dispersed in pure water where it uses the solar energy to split water, and produce hydrogen and oxygen together in the solution. However, in the PEC method, the photoactive material is on the electrode and the process of splitting water is performed in an electrolytic cell with the ability to separate hydrogen and oxygen gases. In the PEC method of water splitting, titanium dioxide (TiO_2) is used as the active material on the electrodes [98, 99]. Other materials, including

semiconductors, have been investigated as a photoelectrode for the conversion of solar energy to hydrogen gas.

An inexpensive and stable oxide photoanode material has been WO_3 . This material is used along with dye sensitized solar cells (DSC) to capture solar photons, because the WO_3 is incapable of separately harvesting the solar photons. The efficiency to convert the solar energy to produce hydrogen gas is known as solar to hydrogen efficiency. The WO_3 photoanode has a maximum solar to hydrogen efficiency of only 8% [100]. A promising photoanode material, which is inexpensive, stable, and capable of harvesting solar photons, is iron (III) oxide (Fe_2O_3), especially $\alpha-Fe_2O_3$ (hematite) [97]. The iron (III) oxide has the capacity to achieve 16.8% efficiency towards the solar to hydrogen conversion [100]. The Solar Fuel Center for Chemical Innovation (CCI Solar) at the California Institute for Technology has been working in the area of solar fuels for many years. They have developed an electrochemical fuel cell with nanorods as photoelectrodes, which can oxidize and reduce water to produce oxygen and hydrogen, sandwiched by a proton conducting membrane [101]. CCI Solar has been undertaking leading research in the area of solar fuels and more information on their solar fuels research can be obtained from their website [102].

Electro-Synthesis of Hydrogen

During the production of solar fuels, hydrogen gas is used as the main raw material to produce hydrocarbons. Hydrogen gas has, however, been used as a fuel for many years to generate electric power, in various types of fuel cells (see section on “Fuel Cells”). Hydrogen gas is also referred to as an energy carrier. So, the production of hydrogen gas by electrochemical methods and its storage

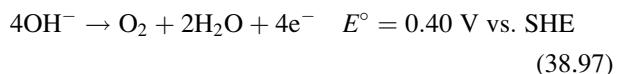
should be considered as one of the methods for electrochemical energy storage. Traditionally, electrolysis is used to split a chemical compound into its elemental forms and water electrolysis has been utilized to produce hydrogen gas. In addition, other starting materials, such as ammonia, urea, and coal particles, are also available to produce hydrogen via electrolysis.

Water Electrolysis

The electrochemistry of water electrolysis is discussed in this subsection (For more details on industrial scale electrolyzers, see section on “Hydrogen and Oxygen Production”). The splitting of a water molecule into hydrogen and oxygen gases with the help of electric current is known as water electrolysis. Initially, nickel electrodes were used as the cathode and anode material for the electrolysis of water because of its low cost. Recent research indicates the use of nickel-based alloys, steel, and nickel-coated or noble metal-coated steel as effective electrode materials [21]. KOH solution is used as the electrolyte for water electrolysis, and is also responsible for the name “alkaline water electrolysis.”

The anode and cathode reactions for the electrochemical splitting of water to produce hydrogen and oxygen are given below:

Anode reaction



Cathode reaction



Overall reaction



The theoretical voltage required to dissociate water into hydrogen and oxygen gases is 1.23 V, whereas the thermoneutral voltage is 1.48 V. Commercially available water electrolyzers operate between 1.6 and 2.0 V. The anode and cathode sides of the electrolyzer are separated by a membrane that allows the ions to pass through but keep the gases separate. Therefore, the hydrogen gas produced using this method does not require further purification as it is almost 100% pure.

The hydrogen gas produced from water electrolysis can be supplied to a fuel cell to generate electric power and water. The reactions taking place inside the fuel cell are opposite to the ones observed in the water electrolyzer. So, combining the water electrolyzer with the fuel cell will result in a net energy or power loss because more energy is

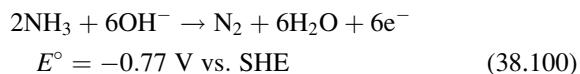
required to split water in the electrolyzer. Additionally, deionized water is necessary for the optimum functioning of the water electrolyzer [103].

Ammonia Electrolysis

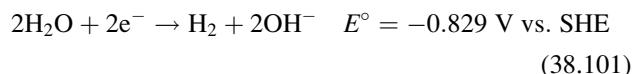
Water is not the only source of hydrogen. There are other chemicals which have a higher atomic weight of hydrogen present, such as ammonia and urea. Ammonia is a colorless gas with a pungent smell. Ammonia is produced by the Haber-Bosch process, in which molecular nitrogen is reacted with hydrogen at high temperature and pressure in the presence of a catalyst to produce ammonia. Ammonia has, however, been found in the emitted gases associated with the fertilizer industry, livestock management, coke manufacturing industry, refrigeration methods, and combustion of fossil fuels [104]. In 2009, the United States was the fourth largest producer of ammonia in the world, as it produced 7,704 thousand metric tons of ammonia [105]. In 2002, the US Department of Energy suggested that 65% of the emitted ammonia comes from fertilizer, livestock, and domestic sources, which accounts for nearly 3.25 million tons of ammonia in the atmosphere [106]. Additionally, ammonia is a pollutant as it can have an impact on vegetation and other organisms [107, 108].

The wastewater from some industries as well as residential community is rich in ammonia. Dissociation of ammonia present in the emitted gases as well as wastewater will help in cleaning up the environment along with the production of hydrogen gas. This rationale motivated the researchers at the Center for Electrochemical Engineering Research (CEER) at Ohio University to study ammonia electrolysis [109]. In 2005, Gerardine Botte, director of the CEER, proposed this new technology for the production of hydrogen gas from the electrolysis of ammonia and since then, there have been a consistent development in this technology [110–118]. During ammonia electrolysis, water present in the cathode electrolyte, a 5 M KOH solution, is reduced to hydrogen gas. On the anode side, 1 M ammonia dissolved in the KOH solution is oxidized to nitrogen gas:

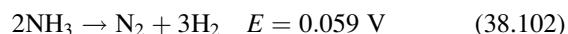
Anode reaction



Cathode reaction



Overall reaction



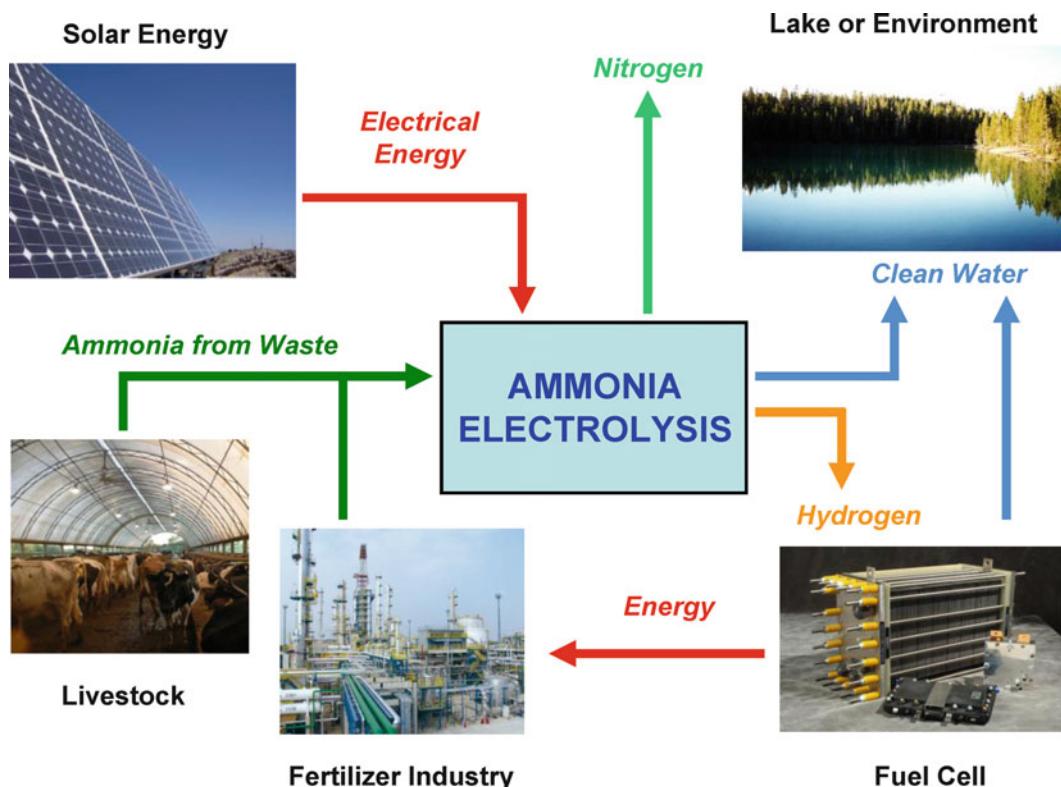


Fig. 38.14 Scheme of ammonia electrolysis along with renewable energy (e.g., solar energy) to remediate ammonia rich wastewater into hydrogen and clean water [143]. The idea of the scheme is to

remediate the wastewater using electrolysis to produce hydrogen gas, which could generate additional energy, and also clean water for eventual use in other applications

The electrolysis of ammonia requires a theoretical cell voltage of 0.059 V, which is minuscule in comparison with that of water electrolysis (1.23 V). If solar energy (\$0.21/kWh) is used to provide the electric current needed for ammonia electrolysis, then the cost for 1 kg of hydrogen produced from ammonia electrolysis will be \$0.90 based on \$175/ton of ammonia. In contrast, water electrolysis using electricity from solar energy would produce hydrogen gas at a cost of \$7.10/kg. So, the production of hydrogen gas from ammonia electrolysis is less energy consumptive, as well as cheaper, than water electrolysis.

One of the goals of the CEER is to develop a scenario in which an ammonia electrolyzer can be used to clean ammonia rich wastewater in order to produce clean water and hydrogen gas for power generation (Fig. 38.14). In Fig. 38.14, the ammonia rich wastewater from industry, livestock, and residential communities are electrolyzed using the electricity from solar energy or any available energy to produce clean water, which can then be returned to bodies of water, and to produce pure hydrogen gas along with nonpolluting nitrogen gas. The industry or residential community can use the energy obtained from the hydrogen gas from fuel cells thereby reducing the demand for oil and

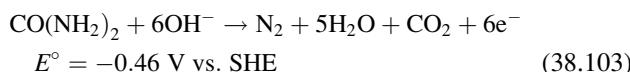
natural gas. In addition to hydrogen production, the electrolysis of ammonia rich wastewater eliminates a pollutant from wastewater and produces clean water, which could be used for various activities. The technology represents a groundbreaking solution for the denitrification of water in wastewater treatment plants.

Urea Electrolysis

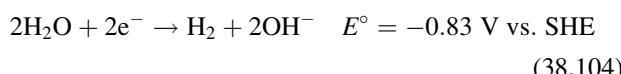
Urea is an important chemical for the mankind as it is used in the production of fertilizer. At the same time, urea is found in wastewater, such as agricultural runoff, as well as in human and animal urine. Even industrial wastewater, especially the wastewater from the fertilizer industry, has relatively high concentrations of urea. The chemical structure of urea ($\text{NH}_2\text{--CO--NH}_2$) has two amine groups attached by a carbonyl group. The presence of the amine group in urea was beneficial for CEER researchers in order to extend the ammonia electrolysis principle to the electrochemical oxidation of urea [119, 120]. Cleaning the urea rich wastewater is important for the disposal of the wastewater in bodies of water. Using the electrochemical approach to remove urea from wastewater has an added advantage of producing high value chemicals, such as hydrogen.

The anode and cathode reactions for urea electrolysis are given below, where 0.33 M urea along with 5 M KOH forms the anode side electrolyte solution and 5 M KOH forms the cathode electrolyte.

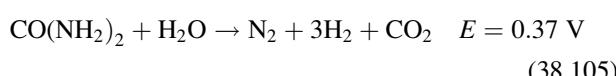
Anode reaction



Cathode reaction



Overall reaction



The electrocatalyst used in the anode electrode for the urea oxidation is nickel, which is oxidized to nickel hydroxide ($\text{Ni}(\text{OH})_2$) in the alkaline solution, which can be KOH. The theoretical cell voltage for urea electrolysis is 0.37 V, which is 70% less energy consuming than water electrolysis [121]. The urea rich wastewater can be remediated using this electrolysis method, thereby producing hydrogen gas, an energy carrier and environmentally harmless nitrogen gas. CEER researchers are working towards developing an electrolyzer which can directly oxidize urine into hydrogen and nitrogen gas. The urea electrolyzer can be used in place of the ammonia electrolyzer in the scheme displayed in Fig. 38.14 in order to demonstrate the possibility of cleaning urea rich wastewater into clean water and producing valuable product as hydrogen gas [119–125].

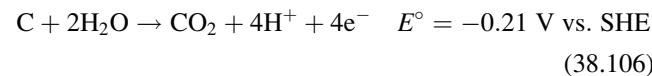
Coal Electrolysis

In the world today, hydrogen gas is typically being produced from fossil fuels, including coal, using the gasification technique. An alternate method to utilize coal for hydrogen production is coal electrolysis, which was proposed by Coughlin and Farooque in the late 1970s, but their research was discontinued due to low oxidation currents [126–130]. Recently, Botte and her collaborators at CEER revitalized and significantly improved the electrolysis of coal for the production of hydrogen [131–139].

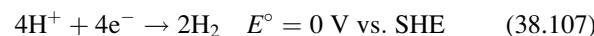
The production of hydrogen gas using the electrolysis technique described until now has been based on the use of an alkaline electrolyte. However, coal electrolysis uses sulfuric acid as its electrolyte; it therefore can be considered an acid electrolysis system. Electrolysis of coal is an excellent alternative method to the coal gasification technique mainly because of the high energy required under the gasification

process (800°C) along with the required purification steps in order to obtain highly pure hydrogen gas. On the other hand, coal electrolysis uses 4 M sulfuric acid circulating in the cathode side, which is separated from the anode side by a membrane. The anode side electrolyte is composed of coal particles mixed with 4 M sulfuric acid as coal slurry. The electrochemical reactions at the anode and cathode electrodes take place at intermediate temperatures (40–108°C):

Anode reaction



Cathode reaction



Overall reaction



The theoretical cell voltage for the overall reaction from coal electrolysis is 0.21 V, which is less than the 1.23 V value associated with water electrolysis. The electrochemical cell used at CEER is known as a continuous electrolytic cell (CEC). Electrolytes for both the anode and cathode side are constantly circulated in order to oxidize a high percentage of the coal particles. The research at CEER has found that the addition of Fe(II)/Fe(III) redox couple to the coal slurry solution increases the rate for the electrochemical oxidation of coal [134, 136, 139]. The CEC used for coal electrolysis has a membrane separating the anode side from the cathode, which has resulted in almost 100% pure hydrogen gas from the cathode compartment. This approach eliminates the need for gas purification equipments.

Once the coal particles have been used in the electrolysis process, the electrolyzed coal is subjected to extraction of liquid chemicals. These liquid chemicals are expected to have high amounts of various hydrocarbons with properties of fuels so as to be termed as liquid fuels. The electrolysis of coal helps in the production of hydrogen gas, a high value chemical, and the solid waste from the electrolysis is further processed to obtain liquid fuels [133].

Summary

The concept of storing energy is as important as generation of the energy itself. Even though there are various methods of storing energy, the most promising methods will be based on electrochemical storage systems. Electrochemical energy storage devices are not limited to batteries, flow batteries,

fuel cells, and supercapacitors. The advancement in rechargeable batteries, such as lithium-based batteries, has improved their usage as electrochemical energy storage devices for varying applications. There are new types of batteries being developed, namely high temperature and flow batteries, which has the potential to be used for large-scale power generation or storage units. Similarly, there are promising developments in the field of fuel cells and supercapacitors to improve the capacity to generate power and store energy, respectively, from these systems.

The idea of storing energy can be extended to the synthesis of the chemicals as well, in which the chemicals are generally used for producing power or energy. In this manner, during the synthesis of the chemicals the energy is stored in the chemical bonds of the compounds formed. On that basis, the electrochemical synthesis of the chemical compounds has been around for more than a century. Synthesis of chemical compounds using electrochemical processes provides precise control over the reaction, which results in higher yield and purity.

In the beginning, the manufacturing of chemicals using electrochemical methods was highly energy consuming and less efficient. These challenges meant that industrial electrosynthesis could hardly be considered a process for energy storage. In the earlier days, the focus of the industry and even the accompanying research was to improve the yield and purity of the chemical compounds produced. Over the years, there has been development and advancement in every aspect of the electrochemical and electrochemical engineering field as well as the other areas of science and technology. With the passage of time, improvements from all of the related fields have been incorporated at different levels (including nanotechnology) of the industrial scale electrosynthesis technology mainly to lower energy requirement and also to increase the yield of the products.

In the modern era, energy requirement for the synthesis processes along with the health and environmental impact of the synthesis routes have equal or even more importance than yield of the product as in earlier times. Consequently, more time and money are spent in the research and development process to improve the synthesis technique using the knowledge, including information obtained from other fields of science, which has resulted in a true multidisciplinary research. This research has focused on understanding the reaction mechanism using available analytical methods even under *in-situ* conditions, developing advance materials through nanotechnology and nanoscience, and systematic use of experimental studies at the laboratory, bench scale, and pilot level, along with theoretical investigations using computational and multiscale modeling methods. This approach to using multidisciplinary research and the involvement of new technologies reflect an encouraging and promising future for electrochemical energy storage systems.

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